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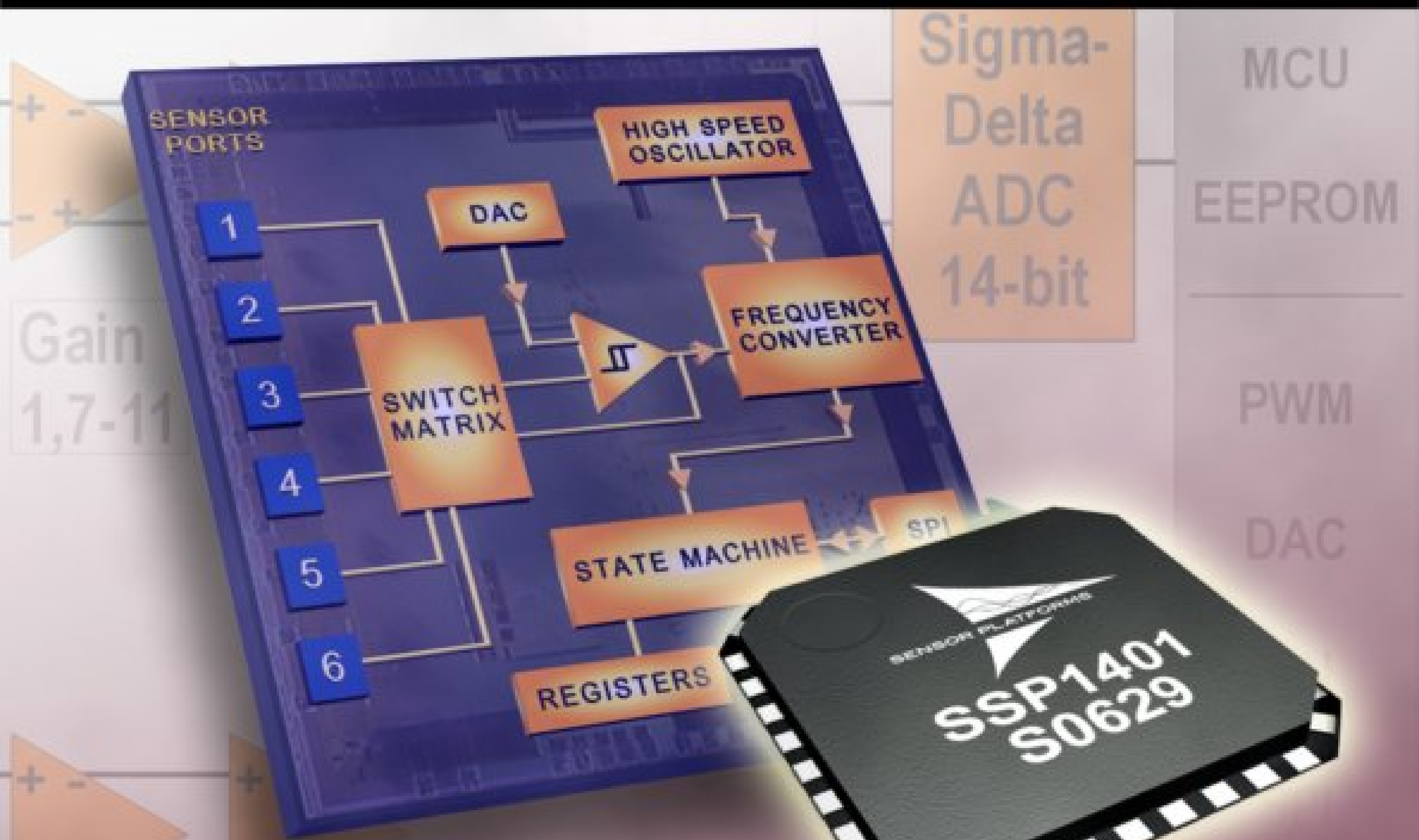

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Effect of SiO_2 Overlayer on WO_3 Sensitivity to Ammonia

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Abstract: Ammonia gas sensing properties of tungsten trioxide thick film sensor was investigated. The doping of noble catalysts such as Pt, Pd, Au enhanced the gas sensitivity. Platinum doping was found to result in highest sensitivity. Remarkable sensitivity enhancement was realized by coating WO_3 thick film sensors with SiO_2 overlayer. Sol gel process derived silica overlayer increased ammonia gas sensitivity for doped as well as undoped sensor. *Copyright © 2010 IFSA.*

Keywords: Ammonia sensor, metal oxide gas sensor, WO_3, sensor, thick film

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1. Introduction

The world awareness about environmental problems and human safety is increasing tremendously with the technological developments, which had resulted in increased demand for sensors. Ammonia is an offensive odor to be eliminated from our working or living environment. The detection of low ammonia concentrations is required in many field of technological importance such as food technology, chemical engineering, medical diagnosis, environmental protection, monitoring of car interiors and industrial process. Semiconductor gas sensors based on n-type semiconducting metal oxides such as ZnO, WO_3 and SnO_2 have been widely used for low concentration of polluting or toxic gases detection.

Tungsten trioxide (WO_3) had been widely investigated as a metal oxide semiconductor for gas sensor applications [1]. Sensor devices in the form of sintered block, thick film or thin film type have been developed or proposed for detecting NO_x, NH_3, H_2S [2-4]. WO_3 films can be operated at elevated temperatures for long periods of time and selectively detect NO and NH_3 in the presence of interference gases such as H_2, CO, CO_2, CH_4 and various other hydrocarbons [5]. Various methods have been adopted for the deposition of WO_3 such as reactive RF sputtering, thermal evaporation, sol gel and other methods. The results indicate that the sensor characteristics strongly depend on preparation techniques and material microstructure [6, 7]. The working principle of these sensors relies on the detection of a change in resistance on exposure to a gas because only the surface layer is affected by such reactions; the sensitivity is strongly dependent on the surface to volume ratio of the material used. This makes the high sensitivity gas sensor prepared by a porous layer through screen-printing possible. To increase the gas sensitivity and selectivity different catalysts promoters have been suggested [8]. Many materials have been added to this sensing material in order to enhance the sensitivity and the selectivity towards NH_3 and NO_x gases. Recently another method was reported for selectivity control using the bilayers wherein the upper layer is used as an effective filtering layer [9, 10]. The use of inert filters covering the sensor surface had been reported to cause no appreciable lowering the sensitivities, enhancing selectivity. This methodology was efficiently used for Pd and Pt doped SnO_2 sensors. An advantage sought with catalytic filters is the burn out of the interfering gases before they can reach the active layers. Therefore only the target gases are able to reach the sensing layer and alter its conductance. In SnO_2 a surface SiO_2 coating is found to enhance the selectivity to hydrogen, because the SiO_2 layer acts as a gas filter to reduce the access of larger molecules such as C_2H_5OH, CH_4, i-C_4H_{10} into the sensing layer [11]. The silica outerlayer is also found to reduce permeation of gaseous oxygen into the sensing layer and hence enhance the gas sensitivity due to suppressed oxygen re-adsorption. Addition of Pt and SiO_2 had been reported to enhance ammonia gas sensitivity for SnO_2 sensor [12], but such investigations in WO_3 gas sensor are lacking, in particular the information is lacking on the effect of silica overlayer with respect to ammonia sensitivity.

In the present work, the effects of SiO_2 overlayer on WO_3 thick film sensor properties are investigated. Ammonia gas sensitivity was measured for undoped as well as noble metal (Au, Pt, Pd) catalyzed WO_3 thick films. The bilayer sensing element of the type WO_3/SiO_2, where in the silica overlayer was derived by a sol gel process, was found to improve ammonia gas sensitivity in all samples.

2. Experimental

WO_3 powder was synthesized by sol gel process. 5 g tungstic acid powder was dissolved in 30 % H_2O_2. The mixture was stirred for 8 h to obtain peroxotungstic acid (PTA). The solution was heated to dryness to obtain precursor powder for WO_3. This powder was calcined at 600 °C for 4 hours in air. Thick films were prepared by screen-printing technique, and tested for their gas sensitivity at various temperatures and concentrations. Thick paste of the powder was prepared in butyl carbitol medium containing a small amount of ethyl cellulose and terpinoel. Pt heater and gold finger contacts were printed and fired on alumina substrate. Sensor films were coated over gold finger contacts by screen printing technique, and sintered at 800 °C for 10 minutes. For doping, calcined powder was impregnated with a solution of Pt, Pd, Au chloride at 0.4 wt % in water. Finally the dried powder was used to prepare sensor. For the overlayer fabrication silica sol was prepared using tetraethyl orthosilicate, ethanol and HCl. A drop of this sol was coated over the sensor surface uniformly. After drying at 125-150 °C for 30 minutes, the sensors were fired at 600 °C for 10 minutes, and furnace cooled.

Calcined powder was characterized by X-ray powder diffraction (XRD) in 2θ range from 20 to 80º using Bruker Analytical X-ray diffractometer equipped with graphite monochromatized CuKα radiation (λ=1.5418Å). The morphologies of the powders were observed by scanning electron microscopy (SEM). Resistivity and sensitivity for ammonia gas was measured using Keithley 2000 multimeter. Gas sensitivity, were measured using a static system. The sensor sample was placed onto an externally heated sample holder and the working temperature of the films was determined with a thermocouple attached near the sensor. The gas sensitivity measurements were carried out in homemade testing chamber. The gas of required amount was injected with a syringe, after testing for the gas the amount of gas was increased to next level. Sample resistance was measured in air and after exposure to ammonia at different concentration. After completing the measurement, the gas is leaked out. To get reproducible and comparable data, each sensor was heated to 450 °C in dry air for 2 hours before measurement. The gas sensitivity (S) is defined as

$$S = R_{air} / R_{gas} , \quad (1)$$

where R_{gas} is the resistance of the sensor after gas exposure and R_{air} is the resistance of the sensor in air.

3. Results

3.1. Structural

Fig. 1 shows the XRD pattern of WO_3 powder calcined at 600ºC for 4 hours. XRD pattern shows many peaks indicating that the material is well crystallized. By performing peak matching with the standard patterns, the powder was identified as WO_3 having monoclinic structure [JCPDS 43-1035]. The diffraction peaks around 2θ= 24° correspond near to monoclinic structure. However the presence of some tetragonal/orthorhombic phase cannot be ruled out, since the lattice parameters of these phases are very close.

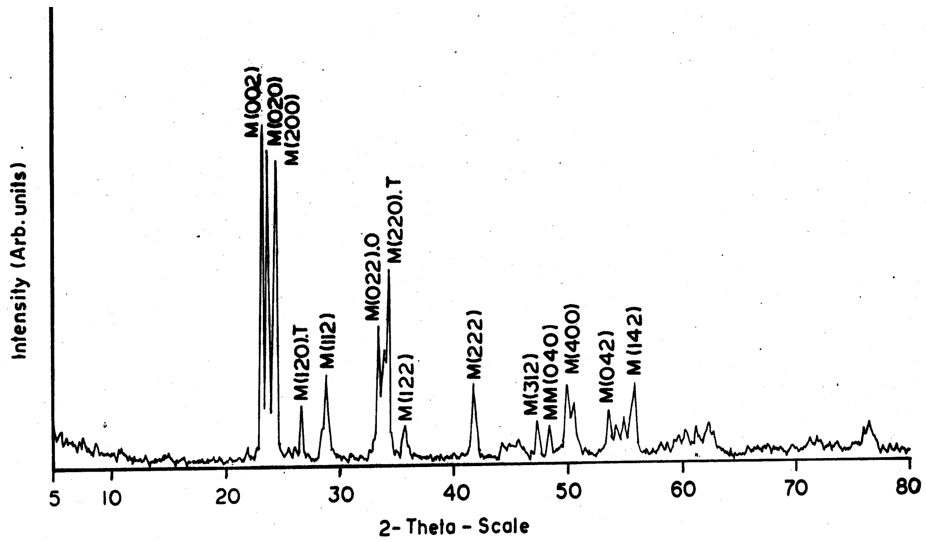


Fig. 1. Powder XRD pattern for WO_3 powder calcined at 600°C (2-hours).

Fig. 2 shows the scanning electron micrograph of a sintered film (800 °C), indicating polycrystalline grain morphology. Agglomerates with sizes ranging from 100 to 500 nm were seen. Highly porous structure was observed showing number of laminar grains separated by large irregular voids. This type of structure was reported to provide high gas sensitivity. After silica overlayer, the samples were fired at a lower temperature 600 °C as compared to the sintering temperature of 800 °C and therefore no change in grain morphology is expected after a silica overlayer**.**

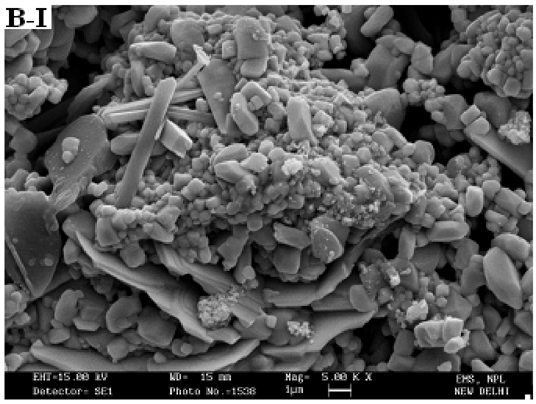
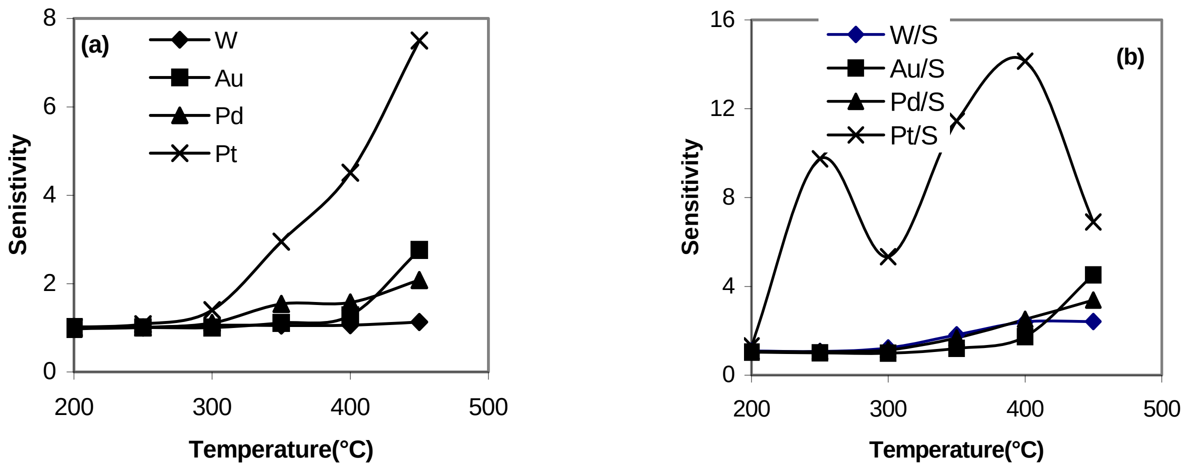


Fig. 2. SEM microstructure of sintered sensor material.

3.2. Gas Sensitivity

The resistance of all the samples decreases drastically when exposed to ammonia. For the temperatures less than 200 °C the gas sensitivity and response being poor the data were not measured. The presence of silica in particular increases the resistance of the layer in air at 300-450 °C. NH_3 is a reducing gas and the exposure to an n-type semiconductor such as WO_3 is known to result in a decrease in resistance. However, the decrease in resistance was small for the undoped material. The results on gas sensitivity for undoped and Au, Pt, Pd added catalysts at 2000 ppm were shown in Fig.3 (a). The sensitivity in general increased on increasing temperature within the range 200-450 °C. Fig. 3 (b) shows the effect of silica overlayer on undoped and Au, Pt, Pd added WO_3 sample. Silica overlayer enhanced the gas sensitivity from 1.1 to 3 for 2000 ppm of ammonia on undoped WO_3 sample. However the sensitivity for undoped WO_3 is still low even after overlayer with silica. It is well known



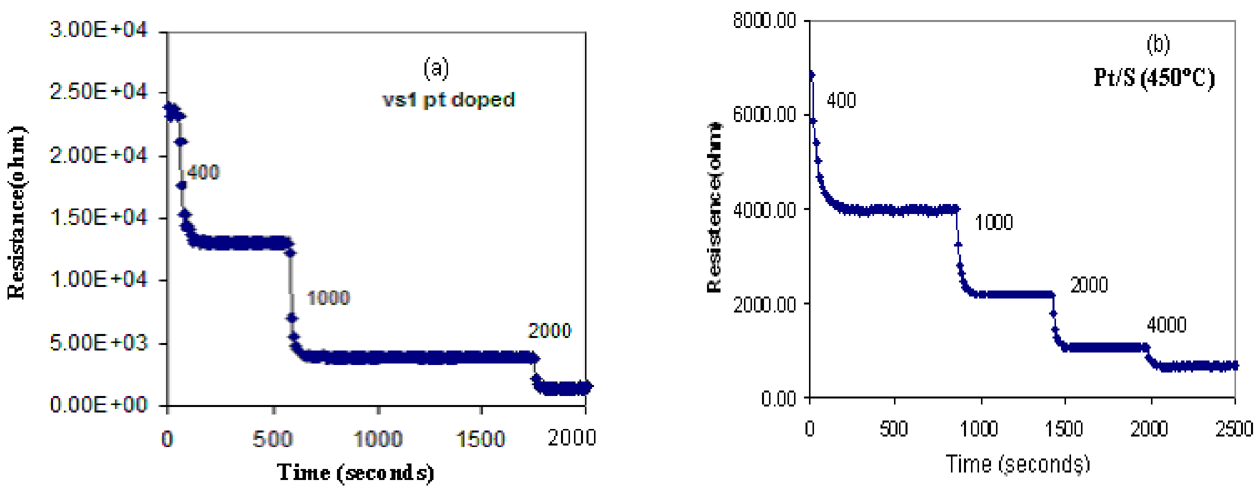
(a) (b)

Fig. 3. Ammonia gas sensitivity for WO_3 sample (a) as prepared (b) after silica overlayer.

that noble metal additives enhance gas sensitivity of metal oxides. Therefore we doped the material with catalysts Au, Pt and Pd to investigate the effect of silica overlayer on these noble metal catalysts added sensors. The incorporation of catalysts (Au, Pt, Pd) enhanced gas sensitivity as shown in Fig. 3 (a, b). Sensitivity for Au doped sensor peaked at two temperatures, 250 °C and 350 °C. After silica overlayer, the gas sensitivity showed enhancement in sensitivity on increase in temperature from 250 to 450 °C. The enhancement in sensitivity for 2000 ppm was from 1.1 to 3 after Au doping. Enhanced gas sensitivity was observed on Au doped sample, wherein ammonia sensitivity increased from 3 to 4.5 after silica overlayer for 2000 ppm ammonia. Palladium doping to tungsten trioxide sensor also increased ammonia sensitivity, similar to Au doping. A sensitivity of 2 was observed for 2000 ppm ammonia at 450 °C. Silica overlayer on Pd doped sensor also showed an enhancement in sensitivity to 3.4. Maximum sensitivity as well enhancement in sensitivity after silica overlayer was observed for Pt doped sensor. The exact reason for this phenomenon is not clear at present. The highest sensitivity of about 7.5 was observed in Pt doped WO_3 at 450 °C for 2000 ppm of ammonia. Silica overlayer showed an enhanced sensitivity of about 14 at 400 °C. Sensitivity was determined for other ammonia concentrations and a substantial improved sensitivity was observed after silica overcoating in almost all samples (doped/undoped) and to different concentrations of ammonia.

3.3. Response Curve

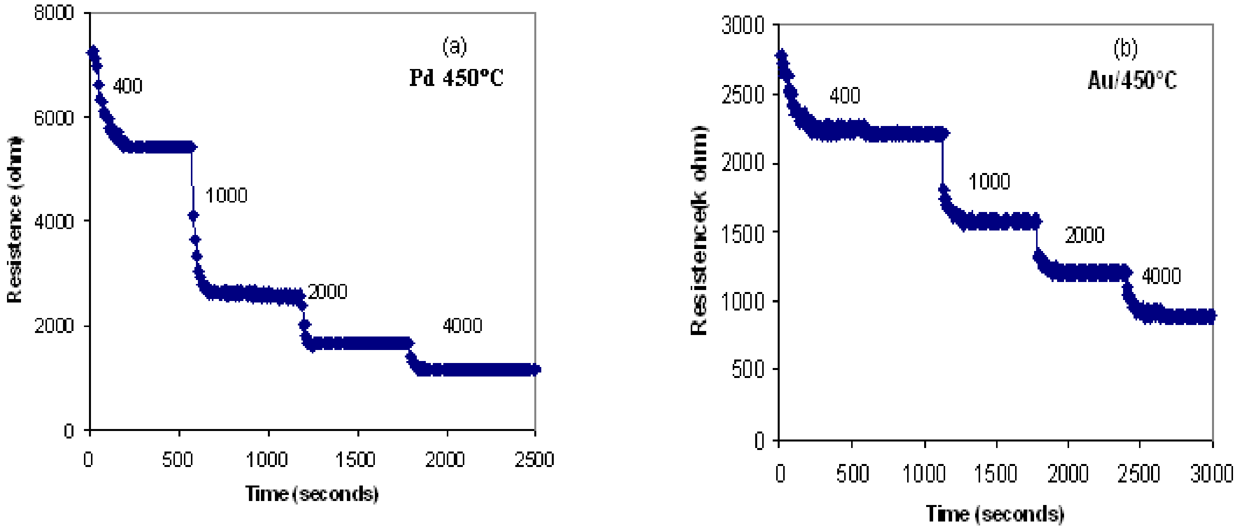
The sensor response time is defined as the time it took the sensor to reach 90 % of its steady state value after exposure to target gas. Fig. 4 (a, b) shows the response curves for Pt doped WO_3 sample before and after silica coating for ammonia gas sensitivity. As shown in the figure on increasing the concentration from 400 ppm to 4000 ppm the resistance drop increases. The resistance decreases within 2 minutes, while after silica coating it takes about one minute to reach equilibrium. Similar curves were obtained for other samples.



(a) (b)

Fig. 4. Response curve for Pt doped sensor (a) as prepared and (b) after SiO_2 overlayer.

Fig. 5 (a, b) shows the response curve for a typical Au and Pd doped sample. In general, a fast response as well as sensitivity enhancement was observed after silica coating. Due to catalysts such as Au, Pt, Pd addition, ammonia sensitivity was increased as compared to undoped sample. It is assumed that in case of catalytic reactions, the ammonia gas is first adsorbed on the catalyst, gets split up into ions and than spillover on the surface and reacts with surface oxygen ions of functional material thereby decreasing the resistance of the sensor and enhancing the response. The response time of ammonia reached about one minute for Pt doped sensor after silica coating for a measurement using 400 ppm concentration. The decrease in response time with silica addition shows that it works not only as a filtering layer but also as a catalytic effect. The sensor exhibits fast response and recovery times as well as quite stable for long time operation. The repeatability is quite good, no appreciable aging was observed. The samples gave a similar response even after storage of 6 months. Further such oxide coating will protect the sample from deterioration. Ammonia gas could easily be detected down to 15 ppm using this sensor.



(a) (b)

Fig. 5. Response curve for (a) Pd doped, and (b) Au doped sensor after SiO_2 overlayer.

4. Discussion

The gas-sensing mechanism is based on the changes in the conductance of WO_3 as a function of NH_3 gas concentration. Ammonia acts as a reducing gas, the carrier concentration in the film rises as a result of the decrease in adsorbed surface oxygen as follows [5]:

$$2\ NH_3 + 3\ O^- \rightarrow N_2 + 3\ H_2O + 3e^- \quad (2)$$

This rise in the electron concentration within the film is reflected as a decrease in resistance.

As shown in the present results, the response to ammonia is higher for noble metal added WO_3 sensors as compared to undoped sensors. According to the literature, noble metal addition forms metallic clusters on the surface of metal oxide grains and produce additional adsorption sites. Noble metals play the catalytic role in the redox process, i.e. store electrons from WO_3 and transfer them to adsorbed reducing agent. They work as catalysts to increase the concentration of O^- species on the WO_3 surface. The kinetics of the reaction depend on the nature of the noble metal, clusters size, temperature etc. Thus noble metal clusters provide the maximum rate of electron exchange between WO_3 matrix and surface species produced by ammonia adsorption. The highest response of Pt doped film may be explained by the high affinity to the reducing agent. Recently Pt loaded Al_2O_3 catalytic filters were reported for screen- printed WO_3 showing highly selective benzene sensitivity [13].

The addition of silica overlayer increased the response to ammonia in all the samples tested. Pure WO_3 samples were more conductive than doped sensors. The addition of silica layer caused a further decrease in conductance for all samples as compared to that before silica overayer**.** Such increase in resistance can be explained by considering the electronic interaction between semiconducting WO_3 grains in contact with the Lewis acid sites (electrons acceptors). The silica layer was deposited through a sol gel process and it is assumed that silica sol will diffuse to the grain boundaries of WO_3 grains, and on firing would convert to SiO_2. The increased sensitivity and air resistance suggests an active participation of silica layer in enhancing ammonia sensitivity. Further, no increase in response or recovery time after the silica coating was observed.

In an earlier work, Joschnick et. al. examined the silica coating effect on WO_3 as microarray to be used for gas recognition [14]. Due to the varying thickness of the silica coating from one side of the array to the other, a different gas response of each sensor element could be achieved. Recently, gasochromic effect of sol gel derived WO_3-SiO_2 films with evaporated Pt catalyst have been reported [15]. It was revealed that the WO_3-SiO_2 composite films exhibited faster coloring kinetics than the WO_3 films annealed at the same temperature [15]. Wang et al. [16] developed SiO_2-WO_3 composites for detection of NO_2 by a spin coating method. It was assumed that the dispersion of fine particles of silica hinders the grain growth of WO_3 leading to a decrease in WO_3 grain size with increasing silica content [16]. The enhanced gas sensitivity to NO_2 had been ascribed primarily to a difference in grain size. Apart from the grain size of the WO_3 film decreases as the amount of silica in WO_3 sol gel is believed to increase the porosity of the composite film and in turn the sensitivity of the sensor. It was assumed that the binders affected the grain boundary (GB) barrier height in the ambience of gas and this phenomenon is related to the chemical nature at the GB. SiO_2-WO_3 film showed the shortest response and recovery times, due to highly porous structure and fast diffusion of NO_2 provided by SiO_2 addition to the composite film.

A significant enhancement in H_2 sensitivity was achieved with a SiO_2 coating film over SnO_2. The SiO_2 coating also induced a drastic slowdown of recovery speed after removal of H_2. Wang et al [12] reported enhanced ammonia sensitivity for Pt and silica doped SnO_2, enhanced stability. Silica was assumed to act as assistant catalyst, and enhanced the activity of Pt catalyst. In another work, the SiO_2 incorporated on the surface of SnO_2 grains was assumed to prevent the neck growth between the grains [17]. In the present work, we have coated silica layer over WO_3 thick film. The samples were already fired at 800°C before coating with silica, which was treated at a lower temperature of 600°C after silica overcoating. Such lower temperature treatment would not change the microstructure or the grain size. However, in all samples the initial resistance before exposure to ammonia gas was enhanced after SiO_2 overlayer as compared to uncoated sample. Thus it might be assumed that the potential barrier height becomes higher with the surface modification compared with unmodified sample. The gas sensitivity of undoped WO_3 also enhanced after silica coating. It appears that silica overlayer modifies the grain boundaries probably by enhancing the number of adsorbed oxygen molecules. Wet impregnation was used to disperse the catalysts well over the WO_3 surface. It is possible that either SiO_2 promotes reduction of NH_3 or SiO_2/WO_3 interface is more reactive than WO_3 alone. It is known that Al_2O_3 as electroactive dopant improves sensitivity of SnO_2 to CH_4 [18]. If silica layer was acting as a passive component than the response time could have decreased, which was not the case observed.

5. Conclusions

Gas sensing properties of WO_3 based screen printed thick films have been investigated. The NH_3 sensing properties of the WO_3 thick film can be improved markedly by addition of Silica overlayer onto the WO_3 film surface. The highest sensitivity was observed for Pt doped WO_3 coated with silica at 450 °C. Such a silica overlayer not only increases the gas sensitivity, decreases the response time also. The response was within 1 minute.

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Guide for Contributors

Aims and Scope

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