TEMPERATURE OPTIMIZATION OF MEMS BASED TUNGSTEN OXIDE (WO_X) GAS SENSORS FOR H_2S DETECTION

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ABSTRACT: Among metal oxide semiconductor, tungsten oxide (WO_3) is an important gas sensing material for the detection of pollutant gaseous species, volatile organic compounds (VOC) and non-hydrocarbon gases such as H_2S etc. Most of these gases, at relative low concentrations, are considered very harmful not only to our health but also to the environment in which we live. These trends aims to develop a low-power consumption, reliable, smart, miniaturized sensing devices, and enable to use battery operated sensors, is an important task. Tungsten oxides show appreciable response at high temperatures and creating them on chip is a difficult task. However by using micro machined silicon platforms has decisive advantage to create such localized hot zones to operate this material for better sensitivity. The present paper deals with the thin film based WO_3 gas sensing material and its response at operating temperatures to detect H_2S gas. In this study we found that the temperature in the range of 100°C to 350°C is a better option to use it as a good sensing material. This higher temperature can be achieved by a micro heater arrangement either on one side of the substrate or an embedded structure within the MEMS suspended platform. In this paper we report the effect of temperature on MEMS based tungsten oxide thin film gas sensor to sense the H_2S gas and the best operating temperature of 200 °C for detecting the pollutant gases such as H_2S using these WO_3 thin films.

INTRODUCTION: In the last decade, tungsten trioxide (WO_3) has been used as one of the most attractive and promising materials for semiconductor gas sensors. The main advantage of this wide bandgap n-type semiconductor certainly lies on its sensitivity to various air pollutants; for instance, NO_x [1-3], O_3 [4,5], H_2S, and SO_2 [6-7]. WO_3 has interesting physical and chemical properties, which make it useful for a wide spectrum of technological applications. For example, tungsten trioxide is an important material for electrochromic [8] and photoelectrochemical devices [9], catalysts [10] and gas sensors [11-13]. Tungsten oxide is nowadays considered as one of the most interesting materials in the field of gas sensors based on metal oxides, as it is shown by the increasing number of publications appeared in recent years. Very good results in the detection of H_2S by sensors based on this material have been reported. Most of them concern WO_3 thin films obtained by physical routes such as sputtering [14,15] or thermal evaporation [16-18]. It is well known that the detection principle of semiconductor metal oxides is based on chemical reduction and oxidation reactions that take place at the sensor surface and that atmospheric oxygen plays an important role in them [19-21]. In [19] Kohl reported that some surface processes for the detection of reducing gases did not require the presence of atmospheric oxygen. The high toxicity of hydrogen sulfide, which has significant negative impacts on health and the environment, has attracted attention to the necessity of monitoring and controlling this gas. With a maximum allowed limit in the atmosphere of 10 ppm H_2S, developing reliable sensors with high sensitivity and also selectivity towards other gases is a real challenge. Metal oxide semiconductors (MOS) have been extensively investigated. For this purpose due to their simplicity, small dimensions and attractive price point. The performance of a solid-state gas sensor is characterized by its sensitivity, stability, and selectivity. The working principle relies on modulation of electrical conductivity due to surface oxidation reduction caused by gas exposure. 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.

WO_3–BASED GAS SENSORS: Certainly, the main asset of WO_3-based gas sensors is connected with its sensitivity to atmosphere pollutants like NO_x [22,26-31], O_3 [23,25,32] H_2S [24,33,34], NH_3 [24,27,35], SO_2 [24], H_2 [27] and C_2H_6O [35]. As other metal oxide based gas sensors, WO_3 is mostly used in the air at atmospheric pressure. In these conditions, it is believed that most of the gaseous species are detected via their influence on the adsorbed oxygen. In particular, the investigations showed that the key reaction of the gaseous species detection involves oxygen ions adsorbed on the surface of the sensor. Thus, at operating temperatures between 200ºC and 500ºC only O^- species which are the most stable reacts with the contaminant gases [36]. Below, it is presented a brief description of the target gases used in this work as well as the reactions produced by the adsorption of these gases on WO_3. Hydrogen sulphide (H_2S) occurs naturally in crude petroleum, natural gas, volcanic gases, and hot springs. It can also result from bacterial breakdown of organic matter or produced by human and animal wastes. Other sources are industrial activities, such as food processing, coke ovens, craft paper mills, tanneries, and petroleum refineries. High concentrations of H_2S may hurt the eyes, nervous system and respiratory system. At low temperatures, it has been suggested that resistance changes, due to H_2S adsorption, occurs as a consequence of the reaction:

$$2\ (H_2S)_g + (O_2^-)\ ads \rightarrow 2\ H_2O + 2\ SO_2 + 3e^-$$

As H_2S is adsorbed, electrons are released into the conduction band and the conductivity increases. In contrast, for high temperature operation, the reaction is:

$$(H_2S)_{ads} + (O^-)_{ads} \rightarrow 2\ H_2O + S + e^-$$

Another mechanism, that can play a role in the gas sensing, is the formation of additional surface oxygen vacancies, created by the interaction of H_2S with lattice oxygen according to:

$$3\ WO_3 + 7\ H_2S \rightarrow 3\ WS_2 + SO_2 + 7\ H_2O$$

This reaction takes place on the surface and involves a reduction of W^{6+} to W^{4+}. Oxygen leaves the surface thereby releasing electrons into the grains so that the conductivity of the film is increased. However, re-oxidation of the vacancies by O_2 results in a competition with the formation of the oxygen vacancies by H_2S [37].

THE EFFECT OF GRAIN SIZE: Xu et al [38] reported a description of the grain size influence on the gas sensitivity. They considered that the gas sensor material is made by a chain of crystallites, which are connected mostly by necks but also by grain-boundary contacts. They state that the resistance of the film is controlled as a function of the relation between crystallite size diameter (D) and the space-charge layer thickness. In this way, three cases were distinguished: $D >> 2L$, $D \geq 2L$ and $D < 2L$ the resistance is controlled by grain-boundaries in the first case, by necks in the second case and by grains in the third case. The sensitivity of the film is higher when the film resistance is controlled by the grains ($D<2L$) when their size is below the critical crystallite size [39]. The details are shown in Fig.-1.

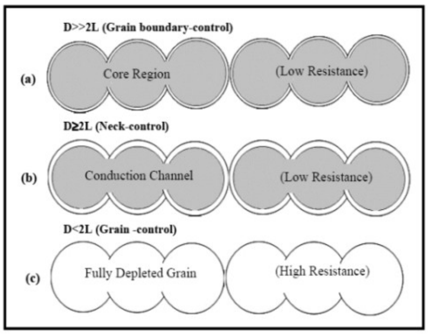

Fig-1: Schematic model of the effect of the crystallite size on the sensitivity of a metal oxide gas sensor: (a) $D>>2L$ (grain-boundary control); (b) $D\geq 2L$ (neck-control); (c) $D<2L$ (grain-control) [38-40].

As soon as a semiconductor is brought into contact with a gaseous medium its surface begins to be covered by the molecules of the gas, i.e. adsorption has set in. The process ceases when an equilibrium between the surface and gaseous phase is established, i.e. when the number of molecules passing from the gaseous phase to the surface per unit time is equal (on the average) to the number of molecules leaving the surface to the gas over the same interval. The presence of the molecules adsorbed by the semiconductor surface changes the properties of the later. Thus adsorption is the agent by which the ambient acts on the surface and, indirectly, on some of the bulk properties of the semiconductor.

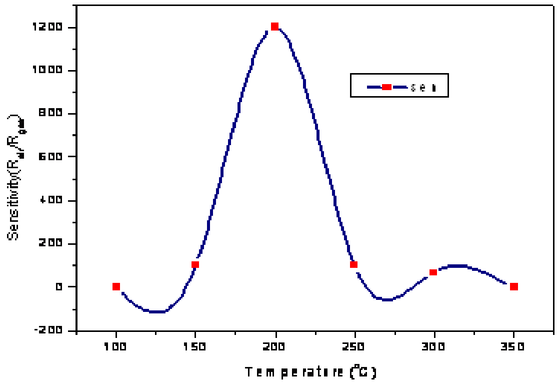

Fig-2: Sensor response of WO_3 to 500ppm H_2S at different working temperature. Tungsten oxides have good response in the range of 100 to 350°C for H_2S detection [35-40].

EFFECT OF OPTIMIZATION TEMPERATURE ON WO_3 THIN FILM GAS SENSOR: In general the sensitivity of the sensors is affected by the operating temperature. The higher temperature enhances surface reaction of the thin films and gives higher sensitivity in a temperature range. A collection of literature survey was carried out for the optimization temperature of tungsten oxide based gas sensor for H_2S gas. With the reference from the published research works we have found that the thin films of the best operating temperature is 200°C for detecting the H_2S gas using WO_3 thin films as shown in Fig.-2.

CONCLUSIONS:

The sensitivity of the tungsten oxide based gas sensor increases with increases the temperature and above optimum operating temperature the sensor response drops off again.

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