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Sensing properties of undoped and Pt-doped SnO_2 thin films deposited by chemical spray

T.V.K. Karthik [a,*], M. de la L. Olvera [a], A. Maldonado [a], V. Velumurugan [b]

[a] *Departamento de Ingeniería Eléctrica-SEES, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, CINVESTAV-IPN, Apartado postal 14740, Mexico DF 07000, Mexico*
[b] *Department of Nanotechnology, VIT University, Vellore, Tamil Nadu, India*

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ABSTRACT

In this work, undoped and platinum doped tin oxide (SnO_2, SnO_2:Pt) thin films were deposited on glass substrates by using the chemical spray pyrolysis technique. The starting solutions were prepared by dissolving tin chloride ($SnO_2 \cdot 5H_2O$) in ethylic alcohol. For doping, platinum chloride ($PtCl_2$) at atomic concentrations of 1 and 3 at% was used. Undoped-SnO_2 thin films were deposited at different temperatures and times, varying between 300 and 500 °C in steps of 50 °C, and 1.5–7.5 min, respectively; whereas SnO_2:Pt films were deposited in the range of 300–00 °C temperature interval at deposition times varying between 5 and 15 min. The film thicknesses and initial sheet resistances were in the range of 30–650 nm, and 150–5 × 10^4 Ω, respectively, depending on the deposition conditions. The crystalline structure of the samples was analyzed by X-ray diffraction (XRD). All the XRD patterns of the films showed a well-defined polycrystalline phase, fitting well with the SnO_2 tetragonal type structure, and a strong dependence on the deposition conditions. The surface morphology was analyzed from Scanning electron microscopy. The effect of the deposition conditions, temperature and time, on the sensing properties of the films was studied in this work. The sensing properties of the SnO_2 films in a carbon monoxide (CO) atmosphere, at different operation temperatures, were tested. According to the sensitivities values, doped films deposited in the 300–400 °C interval presented the best results. SnO_2:Pt films deposited at 300 °C and a [Pt]/[Sn]=3 at% ratio showed the highest sensitivity, around 12, at an operation temperature of 300 °C.

1. Introduction

The composition of the surrounding atmosphere of metal oxides can alter its electrical conductivity due to the adsorption of the different chemical molecules from the environment. In this regard, many metal oxides are suitable for detecting the reducing or oxidizing gases by electrical measurements. The following semiconductor oxides are commonly used for conductometric gas sensors: Cr_2O_3, Mn_2O_3, Co_3O_4, NiO, CuO, SrO, In_2O_3, WO_3, TiO_2, V_2O_3, Fe_2O_3, GeO_2, Nb_2O_5, MoO_3, Ta_2O_5, La_2O_3, CeO_2, and Nd_2O_3, among others [1]. Metal oxides for gas sensing applications can be determined from their electronic structure. According to the electronic structures of metal oxides, they are divided into two categories [2]:

1) Transition-metal oxides (Fe_2O_3, NiO, Cr_2O_3, etc.),
2) Non-transition-metal oxides, which include the following groups:

* Corresponding author.
E-mail addresses: krishnakarthik.tv@gmail.com (T.V.K. Karthik), molvera@cinvestav.mx (M. de la L. Olvera), amaldo@cinvestav.mx (A. Maldonado), velumurugan@vit.ac.in (V. Velumurugan).

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a) Pre-transition-metal oxides (Al_2O_3, MgO, etc.), and
b) Post-transition-metal oxides (ZnO, SnO_2, etc.).

Pre-transition-metal oxides are expected to be quite inert, because they have large band gaps. Neither free electrons nor holes can easily be formed. They are seldom selected as gas sensor materials due to their difficulties in electrical conductivity measurements. Transition-metal oxides behave differently because the energy difference between a cation d^n configuration and either a d^{n+1} or d^{n-1} configurations is often rather small [3]. They can change forms into several different kinds of oxides. Therefore, they are more sensitive than pre-transition-metal oxides to environment.

However, structure instability and non-optimality of other parameters important for conductometric gas sensors limit their field of application. Only transition-metal oxides with d^0 and d^{10} electronic configurations find their real gas sensor applications. The d^0 configuration is found in binary transition-metal oxides such as TiO_2, V_2O_5, and WO_3. The d^{10} configuration is found in post-transition-metal oxides, such as ZnO and SnO_2 [4].

In the field of metal oxide conductometric gas sensors, SnO_2 is by far one of the most studied materials, and also one of the few that has been commercialized in thick film form, due to its good performance in terms of sensitivity and stability compared to other semiconductor oxides. SnO_2 films are highly transparent, chemically inert, and mechanically stable. Apart from research laboratory purposes, SnO_2 films are also utilized commercially in environmental monitoring and industrial electronic sensors [5].

The gas sensing properties of SnO_2 thin films have been probed for different gases like CO, NO_x, H_2S, H_2, CH_4, and CNG (compressed natural gas), etc. [6–8].

Reasons for choosing carbon monoxide (CO) are primarily, its colorless, odorless, tasteless, and initially non-irritating, then it is very difficult for people to detect CO leaks. Secondarily, CO is very often produced in domestic or industrial settings by motor vehicles that run on gasoline, diesel, propane, methane, or other carbon-based fuels and tools, heaters, and cooking equipment that are powered by carbon-based fuels. Exposures at 100 ppm or greater can be dangerous to human health [9]. Thirdly, CO is a product of the incomplete combustion of an organic matter due to insufficient oxygen supply to enable complete oxidation to carbon dioxide (CO_2). Therefore, it is supposed that, during the sensing process, CO combustion process ends when it reacts with the oxygen adsorbed on the semiconductor surface, which alters the surface conductivity of the semiconductor. Finally, the Immediate Danger to Life and Health Concentration (IDLHC) concentration for CO, 1200 ppm, is much higher than for most other toxic gases, making it relatively safe to handle [10].

Doped or undoped-SnO_2 films can be deposited by several methods such as RF Magnetron Sputtering [11], Laser Pulsed Ablation [12], Thermal Evaporation [13], Chemical Vapor Deposition [14], and Spray Pyrolysis [15], among others. It is well known that, the nature of the films deposited by chemical spray deposition is highly affected by the solution and deposition conditions, mainly its grain size, growth rate, and physical characteristics [9]. Spray pyrolysis is extensively used because it is economic, chemically viable, and it is possible the large area deposition.

In order to modify or control the surface properties of the SnO_2 films, introduction of noble metal additives is usually performed. Generally it is assumed that, the metal or metal-oxide additives reside on the surface of the semiconducting gas sensing oxide in form of *dispersed clusters*. The most important effects of the noble metal addition are the increase of the maximum sensitivity and the rate of response, as well as the lowering of the temperature of maximum sensitivity. All these effects arise as a consequence of the promoting catalytic activity when loading with noble metals. A great amount of additives have been studied, being Pt one of the most used. Pt is an excellent additive due its work function value ($\sim$6.35 eV) and chemical inertness. In this respect, previous works have reported that, Pt increases the CO sensitivity [11–15].

One of the main challenges to the developers of metal-oxide gas sensors is obtaining good selectivity. Two common ways for enhancing the selective properties were mentioned by Bochenkov and Sergeev [16]; one is preparing a material that is specifically sensitive to one compound and has low or zero cross-sensitivity to other compounds that may be present in the working atmosphere, and another is based on the preparation of materials for discrimination between several analytes in a mixture, which is usually done either by modulation of sensor temperature or by using sensor arrays. In the primary approach it is usually very difficult to achieve an absolutely selective metal oxide gas sensor in practice, and most of the materials possess cross-sensitivity at least to humidity and other vapors or gases. In this work we have not reported the sensitivities for different gases except for CO. In future we are planning to test for different gases at operation temperatures in order to study the selectivity feature.

The present work is focused on optimization of deposition conditions for depositing good quality SnO_2 thin films by the spray pyrolysis technique for gas sensing applications, particularly for CO. In this respect, we have studied the effect of the deposition temperature and the thickness film, as well as the operation temperature, on the sensitivity under CO gas. The contribution of the present work, compared to those previously reported is that, good sensitivity values at a low operation temperature, 100 °C, were obtained. This is a significantly result, since sensors with a low power consumption, by using SnO_2 thin films processed by a powerful and cost effective technique are possible.

2. Experimental procedure

2.1. Cleaning of substrates

SnO_2 thin films were deposited onto 1 cm × 2 cm glass substrates. The cleaning process consisted of different steps. Firstly, a bath in hot xylene, and then in acetone, both for 10 min were carried out. Right away the substrates were thrice rinsed in deionized water. Secondly, a bath in a hot X1 (1 NH_3OH:1 H_2O_2:5 deionized water) solution was performed for 15 min. After this bath, the