Available online at www.sciencedirect.com
SCIENCE DIRECT
Sensors and Actuators B 109 (2005) 128–134
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

New technology of metal oxide thin film preparation for chemical sensor application

Viacheslav Khatko [a,*], Josep Calderer [b], Eduard Llobet [a], Xavier Correig [a]

[a] *Departament d'Enginyeria Electronica, Universitat Rovira i Virgili, Campus Sescelades, 43007 Tarragona, Spain*
[b] *Departament d'Enginyeria Electronica, Universitat Politecnica de Catalunya, Campus Nord, 08034 Barcelona, Spain*

Available online 3 May 2005

Abstract

The reduction of grain size in metal oxide films is one of the key factors to enhance the gas sensing properties of semiconductor layers. The basic idea introduced here is to create thin metal oxide films with small grain size by using a special regime of rf sputtering from either metallic or metal oxide targets. The regime includes the deposition of thin films with one or several interruptions of the sputtering process. The idea has been checked by preparing WO_3 thin films using reactive rf sputtering from a pure tungsten target. Four types of films were prepared. For the first type a non-interrupted sputtering was used. In the deposition of films type 2, 3 and 4, the sputtering process was interrupted once, two and three times, respectively. It was found that the thickness of the WO_3 films and the sensing properties of WO_3 based sensors heavily depend on the number of interruptions during the deposition process.

Keywords: WO_3 thin films; Deposition with interruptions; WO_3-based sensors; Rf sputtering

1. Introduction

According to Morrison [1], there exist four general ways to increase the selectivity of gas sensors. These comprise using catalysts and promoters [2–6], controlling the operating temperature of the sensors [7–9], including special surface additives for specific surface adsorption [10] and applying differential filters [11–14]. Nowadays, all these approaches are being developed very intensively. In our opinion, in the last few years a new way to prepare gas sensors has appeared. This way is connected with the attempt to find methods that increase the surface area of active layers for chemical sensing. Since the sensor sensitivity is related to the surface–volume ratio of its sensing film, research can be carried out in three directions:

- The first one is related to the investigation of active layers prepared by using nanopowder materials, where particle size is reduced to nanometers. Nanostructure is expected to have a dramatic influence on sensor performance. Many different nano-sized powders and technologies for the preparation of active layers are used to investigate the effect of the nanostructure on their sensing characteristics to different toxic gases [15–18].
- The second direction consists of using special methods of preparation for the surface patterning of active layers. One of such methods implies a process of anisotropic etching to provide a sensor substrate with a much higher surface area [19]. A second method consists of using a porous structure on the base of a highly ordered nanoporous alumina layer [20,21].
- The third direction includes the technologies via with thin films of nanometer grain size can be deposited. As a rule, these technologies are used to obtain thin film gas sensors. For example, active layers with grain size of 1–2 nm could be deposited using rf sputtering or dc magnetron methods [22,23].

One of the basic ideas to create metal films with small grain size is to use successive step-by-step deposition of ultra-thin films resulting in an island structure of two different materials. In this case, at a particular stage of pure metal cluster

* Corresponding author. Tel.: +34 977558653; fax: +34 977559605.
E-mail address: vkhatko@etse.urv.es (V. Khatko).

0925-4005/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2005.03.073

development, clusters of another material can be formed to restrict the coalescence of the metal clusters and the formation of a continuous layer. This technology has been applied with success in the development of catalytic layers for silicon micromachined calorimetric gas sensors [22,23].

A second basic idea consists of using a special regime of thin film deposition by dc magnetron, ion-beam or rf sputtering from metallic or metal oxide targets. Two different special regimes can be used. In the first one the formation of "extra" interfaces in the body of the metal film occurs as a result of the sputtering power density being changed during film deposition. As a rule a low deposition rate is set during the initial stage of film deposition and a high deposition rate is used during the final stage of the deposition. The second regime implies growing the film with one or several interruptions of the deposition process. In this case the "extra" interfaces are introduced into the body of the thin film. During the interruption of the sputtering process or when a sudden change in the deposition rate occurs, an equilibrium surface is formed due to the free surface bond saturation by the atoms from residual atmosphere and/or the structural relaxation of the interface. For the subsequent prolongation of the deposition process, film growth begins over again on the new "extra" equilibrium surface and the average grain size of the film at the surface is smaller than in the original film. It has been shown that this leads to metal films with a decreased average grain size. The first regime has been used for the deposition of Schottky barriers and MOS transistor gates [24,25]. The use of this regime has allowed obtaining the enhancement of catalytic properties of Pt-SiO_2 thin films, as well [26].

Among metal oxide semiconductors, tungsten oxide is a promising material for gas sensing. Several studies have shown that it can be used for the detection of nitrogen oxide (NO and NO_2), carbon monoxide, ammonia vapours, and hydrocarbons. Tungsten oxide films can be deposited by reactive rf sputtering, thermal evaporation and other methods. The results obtained indicate that the characteristics of the sensors heavily depend on the conditions and methods used in their preparation [27–31]. Since grain size is one of the key factors to enhance the gas sensing properties of metal oxide sensors, the aim of this paper is to study the influence of interrupting the deposition process on the sensing properties of WO_3 thin films prepared by rf sputtering.

2. Experimental

The tungsten oxide films were deposited on top of silicon wafers by reactive rf magnetron sputtering using a ESM100 Edwards sputtering system. A metal target of 99.95% purity with a diameter of 100 mm and thickness of 3.175 mm was used. The target to substrate distance was set at 70 mm. The silicon wafers, oxidised in dry oxygen, were held in thermal contact with a holder during the deposition process. The substrate temperature was kept constant during film deposition at room temperature. The sputtering atmosphere consisted of Ar–O_2 mixed gas and its flow rate was controlled by separate gas flowmeters to provide an Ar:O_2 flow ratio of 1:1. The pressure in the deposition chamber during sputtering was 5×10^{-3} mbar. The rf sputtering power was 200 W. These conditions of deposition gave an average deposition rate up to 2.12 nm per min.

Four types of tungsten oxide films were prepared. For the first type a non-interrupted sputtering was used. In the deposition of films type 2, 3 and 4, the sputtering process was interrupted once, two and three times, respectively. A shutter was used to interrupt the deposition process. The total deposition time was 40, 40.5, 41 and 41.5 min, for films type 1, 2, 3 and 4, respectively. The interruption time was set to 30 s. Film thickness was controlled by ellipsometry (PLASMOS 2000) and stylus profilomentry (DEKTAK 3030) and was calculated from AES profiles as well.

The samples used to investigate the gas sensing properties of the films as a function of the number of interruptions during the deposition process were based on silicon substrates. The top contacts to the sensing layers were formed using air dry silver paste (Heraeus AD1688-06). Using this paste the test samples were fixed on the ceramic heater prepared according to the method reported in [32].

The response of the different films to nitrogen dioxide, carbon monoxide, ethanol and ammonia was investigated. The sensors were kept in a temperature and moisture controlled test chamber (27 °C, ±1 °C and 41–43% RH). The sensors were operated at the temperature range from 150 to 300 °C to analyse the effect of working temperature on their response. The resistance of the sensing layers in the presence of either pure air (R_{air}) or the different pollutants (R_{gas}) at the different concentrations was monitored and stored in a PC.

The morphology of the sensing layers was determined by AFM. The sensing layer surface and the chemical element distributions in the samples were examined with a PHI-660 Auger spectrometer operating at 3 kV and using a probe diameter up to 1 μm. Auger electron collection depth was up to 2.0 nm.

3. Results and discussion

3.1. Measurement of film thickness

Table 1 shows the measured thickness of the WO_3 thin films. Two basic tendencies in the thickness as a function of

Table 1
Thickness (nm) of the WO_3 thin film as a function of the number of interruptions of the deposition process as estimated by profilometry and ellipsometry

Number of interruptions	Measurement method	
	Profilometry	Ellipsometry
0	83.2 ± 1.0	81.51 ± 0.11
1	80.0 ± 1.0	65.9 ± 0.61
2	74.0 ± 1.0	55.6 ± 0.33
3	69.5 ± 1.0	–