Chapter 41
Electrochemical Sensors for the Detection of Hydrogen Prepared by PLD and Sol–Gel Chemistry

George A. Mousdis, M. Kompitsas, and I. Fasaki

Abstract Two different series of H_2 sensors were prepared. The first series was based on n-type semiconducting SnO2 thin films, prepared by the sol–gel method. The effect of Au and Pt nanoparticles in SnO_2 was investigated for gas sensor applications. The second series was based on p-type NiO thin films, which were grown by pulsed laser deposition on microscope glass or (100) Si substrates. The effect of substrate temperature and O_2 pressure during the deposition process on the morphological and sensing properties of the films has been investigated. The films were fully characterized. A significant response to a broad range of hydrogen concentrations was demonstrated for both series of films at operating temperatures lower than 200°C.

Keywords SnO_2 · NIO · Thin films · Au · Pt nanoparticles · Hydrogen sensor

Introduction

Nowadays the development of solid-state gas sensors for the detection of inflammable and toxic gases such as hydrogen, carbon monoxide, etc. is a major concern for both human and environmental protection.

Hydrogen is an abundant, renewable, efficient, clean energy source, which produces zero emissions [1]. In the near future it could be used as a city gas or to power cars in the same way as natural gas is used. As an industrial gas, it is currently used in a large number of areas, e.g. chemistry (crude oil refining, plastics, as a reducing environment in float glass industry, etc.), food products (hydrogenation of oils and fats), semiconductors (as a processing gas in thin film deposition and annealing atmospheres), and transportation (as fuel in fuel cells and space vehicle rockets).

All these applications require the development of hydrogen sensing devices that allow safe control of the gas usage. Devices capable of detecting hydrogen

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concentrations below the lowest explosion limit (LEL) of 40,000 ppm [2] have become indispensable to prevent explosions. A promising approach in the field of solid-state sensing devices is to use electrochemical gas sensors based on semiconducting metal oxides (MO), utilizing novel gas sensing materials [3].

Metal oxides, in particular tin dioxide, are widely used as a basic material for the preparation of gas sensing devices [4]. The effect of the addition of metallic particles on the gas sensing properties of metal oxides has been widely studied, but the results depend on the experimental conditions and method of fabrication [5]. Although n-type transition metal oxide semiconductors (such as SnO_2 and ZnO) have already been investigated as gas-sensing materials, the sensing properties of p-type semiconducting oxides have received significantly less attention.

Nickel oxide (NiO) is widely considered as a model p-type semiconductor. Due to its excellent chemical stability, NiO films have a broad range of applications as catalysts [6], electrochromic display devices [7] and fuel cells [8]. Moreover, recent studies have shown that NiO thin films are attractive sensing materials in gas and humidity detection devices [9].

MO thin films can be deposited by different techniques, including chemical self-assembling, sol–gel, rf sputtering, dc sputtering and pulsed laser deposition (PLD). We have used an alkoxide sol–gel method to prepare SnO_2 thin films, undoped or doped with Au and Pt nanoparticles. Additionally, undoped NiO thin films were prepared by PLD. All films prepared were tested as H_2 sensors, and the influence of preparation conditions to the sensing properties were studied.

Experimental

Synthesis of SnO_2 Films

Starting point was a mixture of tin isopropoxide in isopropanol and an ethanolic solution of $HAuCl_4$ (or H_2PtCl_6) [10]. This solution was hydrolyzed and aged by stirring at room temperature (r.t.) for 24 h. After spin-coating on glass or Si substrates, the tin oxide gel films were dried at r.t. for 1 day and heat-treated for 2 h at 510°C in air. The content of the metals (Au and Pt) in the SnO_2 matrix was 5 wt%.

Synthesis of NiO Films

Undoped NiO films were grown by PLD in a stainless steel vacuum chamber [11]. A Ni foil (purity 99.999%) was used as a target, placed on a movable vacuum-compatible, computer-controlled XY translator and irradiated by a Quantel Nd: YAG laser ($\lambda = 355$ nm) at a repetition rate of 10 Hz. The NiO films were

deposited on heated Si or glass substrates. Two series of films were grown. The first was deposited at an O_2 pressure of 10 Pa at room temperature, 200°C and 400°C, the second at 400°C and O_2 pressures ranging from 5 to 50 Pa.

Characterization and Sensing Studies

The films were characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD) and ellipsometry.

Hydrogen sensing tests were performed in an aluminum vacuum chamber [12]. The chamber was evacuated down to 1 Pa, filled with dry air at atmospheric pressure. The samples were resistively heated to operating temperatures of 147–180°C. The films were tested at hydrogen concentrations in the range of 10,000–500 ppm. The hydrogen concentration was calculated based on the partial pressures of the sensed gas and air inside the chamber. A bias of 1 V was applied, and the current through the film was measured with a Keithley Mo. 485 Picoammeter. The response r is defined as $r = (R_o - R_s)/R_o = (I_s - I_o)/I_o$, where R_s and R_o are the sensor resistivities with and without gas, respectively. Current changes are therefore a measure for hydrogen sensing.

Results and Discussion

SnO_2 Films

Structural and Morphological Properties

Thermogravimetric analysis showed that heating at 500°C evaporates or burns all the organic components and reduces the $HAuCl_4$ or H_2PtCl_6 to metallic Au or Pt. XRD characterization of the films revealed that both types of SnO_2 samples are polycrystalline. The presence of Au and Pt clusters in the films seems to induce some changes in the texture of the films [10]. SnO_2–Au films have a clear tendency of texturing in the [101] and [200] crystalline directions of the tetragonal rutile structure. SnO_2–Pt films show a weaker tendency for texturing with a preferred orientation towards the [200] direction [10].

According to scanning electron microscopy (SEM) characterization, all SnO_2 samples show the presence of a granular film structure with randomly distributed and shaped particles on the surface. In the case of the SnO_2–Au sample, the particles are mostly irregularly shaped with dimensions of a few hundred nanometers, as shown in Fig. 41.1 (ignoring some quite big features of μm dimensions attributed to dust formation and impurities during sample preparation for SEM). In the case of SnO_2–Pt, the top features are clearly hexagonal faceted (Fig. 41.1. insert).

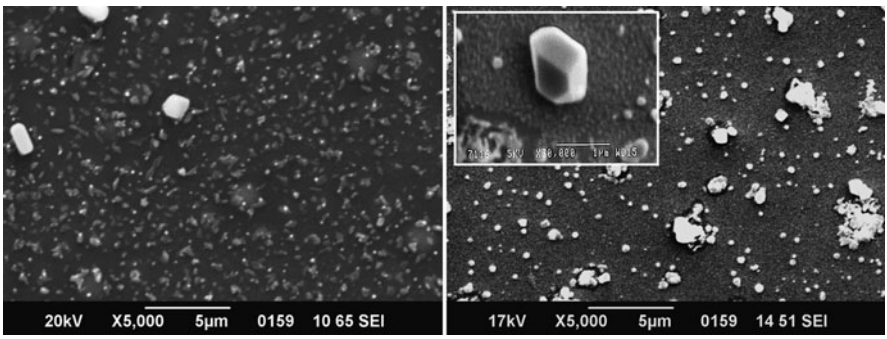

Fig. 41.1 SEM image of SnO_2-Au (*left*) and SnO_2-Pt (*right*) thin films

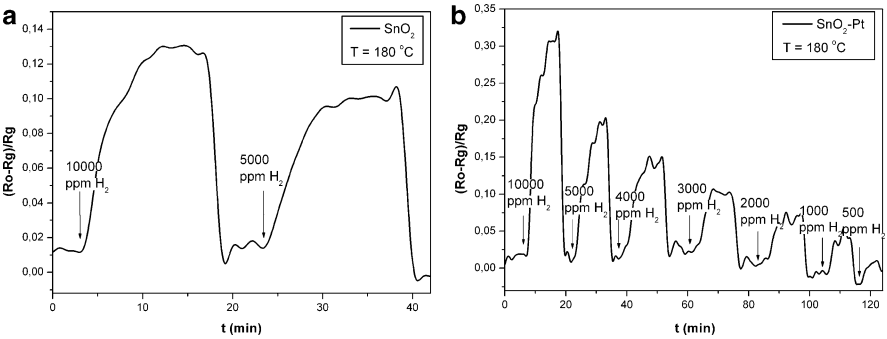

Fig. 41.2 Response of SnO_2 and Pt-SnO_2 thin films at 180°C

Hydrogen Sensing

SnO_2 films without metal nanoparticles respond only at temperatures above 180°C and hydrogen concentrations higher than 5,000 ppm (Fig. 41.2a). The presence of Pt in modified SnO_2–Pt films distinctly enhanced the relative response, the detection limit was lowered down to 500 ppm (Fig. 41.2b). The SnO_2–Au sensor response exhibits a dramatic increase by 50 times at the same temperature (Fig. 41.3a). Furthermore the working temperature can be lowered down to 85°C (Fig. 41.3b).

NiO Films

Structural and Morphological Properties

XRD analysis of the samples prepared at r.t., 200°C and 400°C showed that the film deposited at r.t. is poorly crystallized. When increasing the substrate temperature, the NiO lines become narrower and their intensities increase, indicative of an

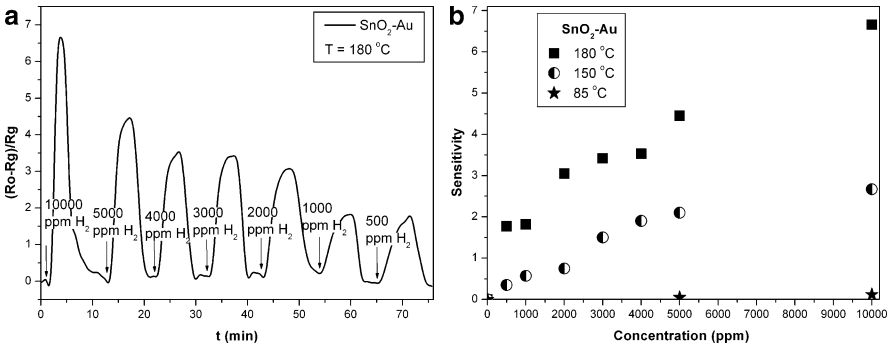

Fig. 41.3 (**a**) Response of Au-SnO_2 thin films at 180°C for 10,000–500 ppm H_2; (**b**) at different temperatures for 10,000 ppm H_2

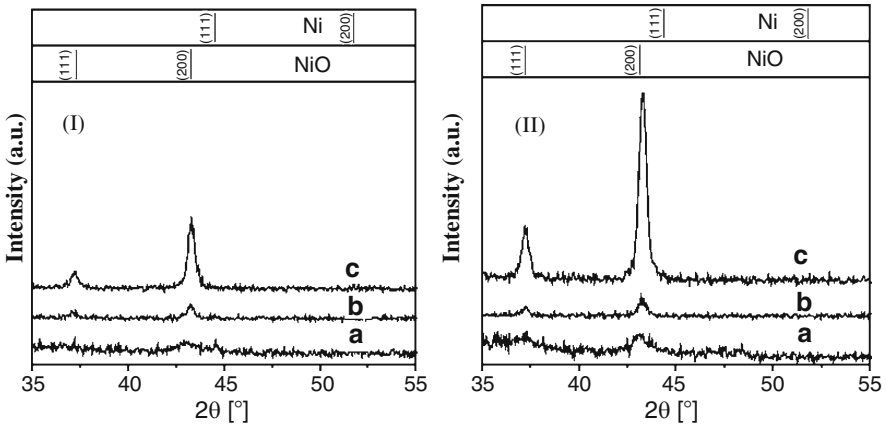

Fig. 41.4 X-ray diffractograms of NiO thin films grown on Si at r.t. (**a**), at 200 (**b**) and 400°C (**c**); (I) without postdeposition heat treatment; (II) after post-deposition heat treatment at 500°C for 3 h

improved crystallinity (Fig. 41.4I). Annealing at 500°C for 3 h increases the crystallinity mainly for the films prepared at 400°C (Fig. 41.4II). Similar results were obtained by AFM.

Ellipsometric measurements of the NiO films prepared at 400°C at different O_2 pressures showed that by increasing p_{O2} the thickness of the film decreases while the roughness increases (Fig. 41.5a). SEM images showed that at low p_{O2} Ni nanoparticles are present due to an incomplete reaction of Ni with O_2 (Fig. 41.5b).

Hydrogen Sensing

All films responded to the presence of H_2 at 180°C. The response of the first group of NiO films depends strongly on the preparation temperature (Fig. 41.6a). The best response was observed for the samples prepared at 400°C (Fig. 41.6a). According to

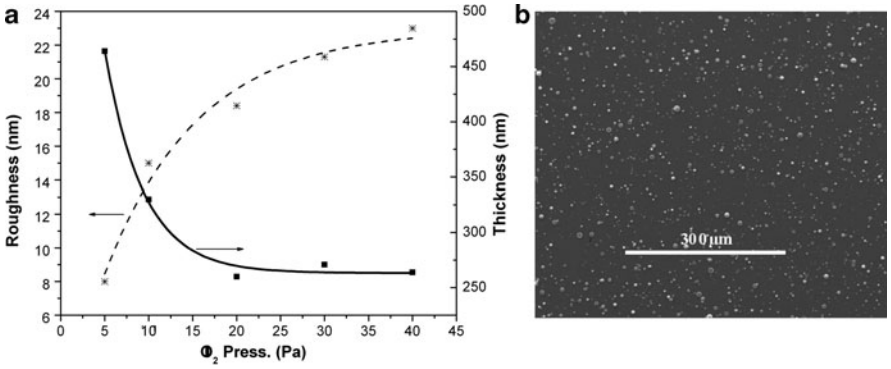

Fig. 41.5 (**a**) Plot of roughness and thickness of NiO films as a function p_{O2}; (**b**) SEM image of a NiO film prepared at 5 Pa O_2 pressure

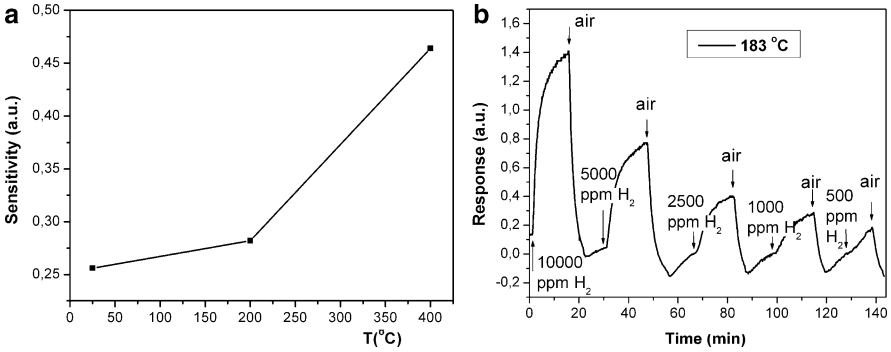

Fig. 41.6 (**a**) Response of NiO thin films at 180°C to 10,000 ppm H_2 as a function of the preparation temperatures; (**b**) Response of NiO thin films prepared at 400°C and 40 Pa O_2 pressure at 180°C operation temperature to 10,000–500 ppm H_2

previous result and the structural and morphological studies of the second group the best sensor was deposited at 400°C and 40 Pa O_2 pressure. This film showed a very good linear response at 180°C for H_2 concentrations of 10,000–500 ppm.

Conclusions

The introduction of Au and Pt nanoparticles in SnO_2 thin films increase their H_2 sensing properties. In particular, Au nanoparticles decrease the working temperature of the sensor to 85°C while the response increases more than 50 times. NiO thin films can also be used as H_2 sensors. Their sensing properties, crystallinity and morphology strongly depend on the growth conditions. Optimized sensing properties can be achieved by deposition at 400°C and 50 Pa O_2 pressure.

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