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A novel ozone detection at room temperature through UV-LED-assisted ZnO thick film sensors ☆

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ABSTRACT

In this work a novel ozone detection at room temperature (RT) has been investigated. Two functional materials, ZnO and $(W_{0.9}Sn_{0.1})O_{3-x}$ (WS10) oxides, have been synthesized to prepare thick film gas sensors, both used in conventional heated mode as well as at RT assisted by UV irradiation. As a source of light, a light emitting diode (LED) of 400 nm peak wavelength was used. Under typical operating conditions of the UV-LED, the radiation flux density ϕ over the sensor was of about $5 \cdot 10^{17}$ photons/cm^2. Powders and films have been characterized by means of TG-DTA, SEM, TEM and XRD. Finally, electrical measurements have been performed on sensing films with the aim to compare conductive properties, surface barrier heights and ozone sensing features with and without UV irradiation. Despite the fact that two types of conventional heated sensors offered quite similar results with respect to ozone sensing, it turned out that, at RT and with the assistance of UV light, ZnO behaved excellently fast detecting ozone at concentrations down to 10 ppb, while for WS10 under the same operating conditions an opposite result was observed, i.e. very low response and long response time.

1. Introduction

Over the years, the widespread of technological applications, such as heterogeneous catalysis, gas sensing, photocatalysis, piezoelectricity, optoelectronics, photovoltaic conversion, etc. have been driven to an extensive investigation on semiconductor metal oxides (MOX) [1–3]. The recent emphasis given to the research on nanostructures and the advent of modern nanotechnologies have opened the way to novel electrical, mechanical, chemical and optical properties [4–6]. Especially for gas sensing, a large variety of nanostructures in a form of nanoparticles, nanowires, nanobelts, nanorods or nanotetrapods have been synthesized [7–10]. In particular, in [10] nanoparticles and nanotetrapods-based thick films have been compared as gas sensors towards some gasses and among them, ozone.

Among the metal oxides semiconductors, ZnO, pioneering material in gas sensing, has been afterward abandoned, recently rediscovered and widely studied. ZnO is a very attractive functional material both for its great variety of properties and the possibility to synthesize it in an enormous amount of nanostructures [10–12]. These wide-ranging features of ZnO promoted research in many applications, such as light emitting or laser diodes, transparent conducting oxides (TCO), hybrid solar cells, cantilevers production, photocatalysis, piezoelectric applications, etc. [13–16].

The behavior of zinc oxide as an n-type semiconductor (band gap of 3.37 eV) is due to lattice defects, in particular oxygen vacancies acting as electronic donor levels. Moreover it exhibits high exciton binding energy (60 meV), which is responsible for an efficient UV emission (~380 nm).

Recently, with the aim to lower the sensor working temperature, many studies on the exposure of metal oxide sensors to UV light have been performed [17–22]. The basic idea arises from the fact that some metal oxides, known for their good sensing capabilities, also show photocatalytic properties, the photo-generated carriers promoting chemical reactions with the adsorbed species on the semiconductor surface. However, a few experimental works have been devoted to understand the sensing mechanism in semiconductor metal oxides under UV irradiation (see for instance [20,23,24]).

This work aims to study the effect of light on different phenomena, such as the ozone detection at room temperature, the recovery time in dynamical measurements and the influence of the humidity in ozone detection. Moreover, some hypotheses on the phenomena occurring in the semiconductor have been examined. Finally, to get a wider view of the problem, two functional materials, ZnO and WS10 (a solid solution of W and Sn oxides, with Sn:W = 10:90) both previously successfully tested as ozone sensors, have been investigated with and without UV light.

☆ In memory of Prof. Giuliano Martinelli, wonderful person and eminent scientist.

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2. Experimental

2.1. Powder synthesis and film preparation

To grow the functional materials in form of nanometric powders, a traditional sol–gel route has been followed.

2.1.1. ZnO synthesis

10 g of $Zn(NO_3)_2 \cdot 4H_2O$ (Aldrich) was dissolved in 18 MΩ·cm deionized water. The precipitation of the white $Zn(OH)_2$ has been carried out adding 12 ml of ammonia solution (28%, Carlo Erba Reagents) dropwise under continuous stirring. The pH of the final solution reached 7.5. The reaction mixture was kept at the temperature of 50 °C in an ultrasonic bath for 3 h. The product was filtered by gravity, washed several times with water, dried at 100 °C overnight in an oven, then calcined at 450 °C for 2 h. The ZnO yield in the chemical reaction was around 90%. The yield is the ratio between the weight of the compound produced in the chemical reaction with respect to the weight of the compound which could be produced in the same chemical reaction in case of complete conversion of reactants to products.

2.1.2. WS10 synthesis

A solution of Tin(II) 2-ethylhexanoate (Sigma) dissolved in the minimum amount of 1-butanol (Carlo Erba Reagents) was added to a 0.2 M solution of WCl_6 (Aldrich) in absolute ethanol (Carlo Erba Reagents) (Sn:W = 10:90 molar ratio). In order to catalyze the hydrolysis process, 1 ml of water diluted HNO_3 solution (pH = 1) was added dropwise under continuous stirring. The solution was kept at 50 °C in an ultrasonic bath for 3 h. The resulting white/yellowish powder (the precursor of the final oxide) was filtered by gravity and washed several times in ethanol. Then the product has been dried at 100 °C overnight in an oven and afterwards calcined at 550 °C for 2 h. The yield in the $(W_{0.9}Sn_{0.1})O_{3-x}$ oxide was around 85%. For both materials, the calcination temperature was determined by TG/DTA analysis (TG/DTA Netzsch STA 409) performed at 20 °C/min in natural air flow.

ZnO and WS10 oxides have been used to screen-print sensing layers onto miniaturized alumina substrates. In order to correlate the film structure with the sensing behavior (with or without UV irradiation), the films of both materials were submitted to equivalent thermal treatment (firing) at 650, 750 or 850 °C for 1 h in a muffle furnace.

2.2. Powders characterization

The crystalline phase of the powders was investigated by X-Ray Diffraction (XRD) using a Philips PW 1830 vertical diffractometer with Bregg-Brentano geometry (Cu Kα radiation, 40 kV, 30 mA) provided with a graphite monochromator along the diffracted beam. Diffraction patterns were collected over the range 10–120° (2θ) with steps of 0.02° and 10 s of dwell time. XRD data were elaborated using a Rietveld analysis program FullProf (release 2006) [25].

2.3. Film characterization

The morphology of all the films was observed using scanning electron microscopy (SEM, model EVO 40, Carl Zeiss).

For the electrical characterization, the sensors have been placed in a sealed test chamber and tested for ozone sensing using the flow-through technique, in dark or assisted by UV light (400 nm of wavelength corresponding to a photon energy of 3.1 eV). This energy, being comparable with the band gap of both semiconductors (ZnO = 3.37 eV; WS10 ~3 eV), should be sufficient to create photo-generated electron–hole pairs. As source of illumination, UV-light emitting diodes (UV3TZ-400-30 LEDs by BIVAR) were used (see in Fig. 1 the photodiode response proportional to the UV-LED power spectral density). A small metal tool was specially made to maintain in each experiment the same position between UV-LED and sensor so that no change in irradiance on the sensing layer occurred. Using this experimental setup under the typical operating conditions of the UV-LED, the radiation flux density ϕ over the sensor is about $5 \cdot 10^{17}$ photons/cm^2. No variation in test methodology was introduced when the sensors were irradiated by the LEDs, differently from other papers in which, prior to ozone exposure, a procedure of photoreduction–oxidation cycles, has been performed (see, e.g., [26]). Just after the LEDs have been switched on, sensors have been left under continuous UV irradiation leaving enough time for the conductance to stabilize. After that, the measurements have been performed as usual.

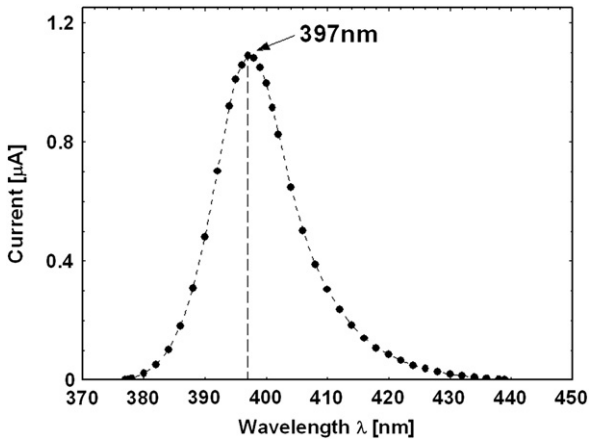

Fig. 1. The photodiode response proportional to the UV-LED power spectral density.

The conductance measurements were carried out maintaining a constant flow of 0.5 l/min when the carrier gas (air) was dry or wet (RH 50%), while the test gas flow was 1.5 l/min in case of air and ozone mixtures. Dynamic responses of sensing films were obtained in presence of ozone by varying the operating temperature from 400 to 650 °C or at room temperature, when the sensors were assisted by UV light. The concentration of ozone, if not differently specified, was always 70 ppb.

The conductance measurements were also performed as a function of temperature (300–900 K) in dry or wet air and in dry or wet air–ozone mixtures. Moreover, to determine the intergranular energy barrier, i.e., the difference in energy between the bottom of the conduction band at the surface and that in the bulk, temperature-stimulated conductance measurements, which consist in measuring conductance as a function of time after a fast temperature variation, were also carried out with a procedure described elsewhere [27–29].

3. Results and discussion

3.1. Structural and morphological characterization

XRD patterns showed ZnO powders with hexagonal wurtzite structure (space group $P6_3mc$), while WS10 exhibited monoclinic structure (space group $P2_1/n$). The Debye–Scherrer formula was used to evaluate the crystallite size of as grown powders of 40 nm for ZnO and 25 nm for WS10.

The size evolution with temperature is reported in the SEM micrographs, in which morphological characterization as a function of firing temperature (650, 750 and 850 °C) has been carried out (see Figs. 2A, B, C and 3A, B, C, for ZnO and WS10, respectively). It can be observed that the morphology of the sensing layers suffers from the grain coalescence, much more evident in WS10 than in ZnO. Indeed, in tungsten trioxide the usual increase of average dimension of the grains with temperature is particularly exaggerated. With the aim to limit this effect, WS10, mixed (W, Sn) oxide with Sn:W = 10:90, has been synthesized as described above. The result was satisfying.