

Evidence of a surface effect of UV light on WO₃ thick-film gas sensors

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Abstract

The electrical conductance of a tungsten trioxide (WO₃) thick-film gas sensors under UV illumination has been investigated. Measurements have been performed in two different environments: in pure nitrogen and in dry synthetic air. The effect of light on the electrical behavior has then been evaluated and interpreted. In particular, the observed increase in conductance after illumination of the surface is expected to be due to interband electronic transitions, since the bandgap of the material is smaller than the energy of the incident photons. An evidence for strong contribution of surface chemical processes to this variation, through surface barrier modulation, is given in this work.

Key words: Tungsten oxide, photo-catalysis, surface effects, conductance

Introduction

Gas sensors based on nanostructured semiconductors oxides have proven to be extremely sensitive to even very low gas concentrations, down to the ppb level [1-4]. Important features like sensitivity, stability, reproducibility of the response and reliability are continuously studied and improved. Progresses in basic understanding of the physics of these nanostructures and their sensing principles are required in order to optimize them when operate as gas sensors.

During the last years, several works have focused on the photo catalytic behavior of some metal oxides nanostructures employed in gas sensing [5,6], due to the fact that these materials show good sensing capabilities that can be also activated by light, other than temperature. While several materials have been investigated specifically for various target gases, few works investigated on the mechanisms behind the conductance changes shown after the illumination of the surface. WO₃ is a good candidate to investigate in this direction, because it shows a strong photo catalytic behavior, which stimulates the gas sensing at room temperature. Interesting experimental results shown in this work highlight the importance of the surface contribution to these conductance changes.

Experimental

Nanometric WO₃ powders have been synthesized through the following chemical route. Commercially available materials and solvents were used without further purification. A solution of 8 mmol of WCl₆ in EtOH abs (Carlo Erba) and PTN (0.08M in EtOH abs) resulted in a paramagnetic blue W(V) complex, whose stoichiometry has not been completely clarified. After a warm treatment in a sonic bath, the solution was stationary for 2 h at room temperature and a precipitate was formed. The blue powder was dried and then annealed at $T = 850\text{ }^{\circ}\text{C}$ for 1 h, leading to a yellow powder with homogeneous and fine grain distribution. The synthesized powder was calcined at $650\text{ }^{\circ}\text{C}$ for 2 h. Structural and morphological characterizations were performed through X-ray diffraction technique (XRD, Philips PW 1820/00, using a Cu K radiation with $\lambda = 1.54\text{ \AA}$, 0.02° step size, integrating 10 s per step) and scanning electron microscopy technique (SEM, Leica Cambridge Stereoscan 360). In Fig. 1 a SEM image of the powder is shown, from which we deduced an average grain size of 50-60 nm. In order to deposit the sensitive layer, the powder has been screen-printed onto an alumina substrate, equipped with gold contacts and a heater, using α -terpineol as organic vehicle together with a small percentage of glass frit to improve the adhesion to the substrate. Then the film has been finally fired at

650°C for 1 h in air. After thermal treatment the thickness of the layers was measured at approximately 25 nm.

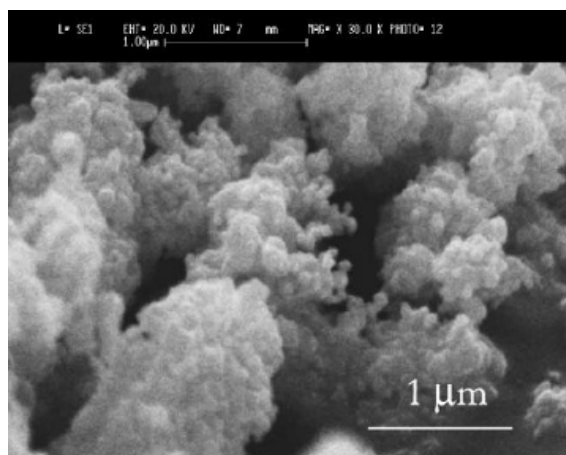


Fig. 1. SEM image of the WO_3 powder.

In this work the heater has not been used. Instead, the conductance of the sensor has been investigated at room temperature, with the light as the only current enhancer.

The conductance measurements have been performed by means of the flow-through technique in a sealed test chamber, provided with a borosilicate window, which allows the transmission of 87% of the incident light. A 400 nm LED has been used as light source, which provides a very narrow emission spectra at a very low cost. The set-up of the experimental apparatus has been achieved placing the LED outside the chamber and focusing the light onto the surface of the sensor through an optical system, as shown in Fig. 2. The focused beam of light had an area corresponding to a circle of 1.5 mm radius, enough to cover the whole film, since it is a square of 2 mm side.

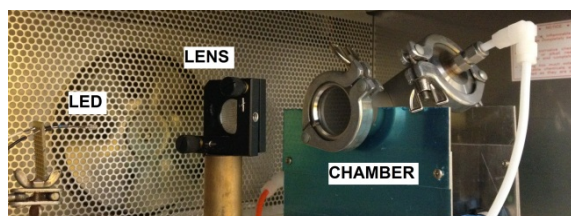


Fig. 2. Experimental apparatus.

Conductance measurements have been performed following this route: after stabilization of the sensor's signal in dark, the LED has been switched on, and switched off after stabilization has been reached (hours). A series of on-off cycles have been performed in a pure nitrogen environment and in dry air.

Results and discussion

The on-off cycles of the LED resulted in a very different behavior of the conductance of the film in the two different atmospheres (air and pure N_2). In Fig. 3a) and 3b) we reported, with the same scale, the ratio between the instantaneous conductance and its value in dark at the beginning of the measurement, as a function of time, for both environments, in other terms with and without oxygen.

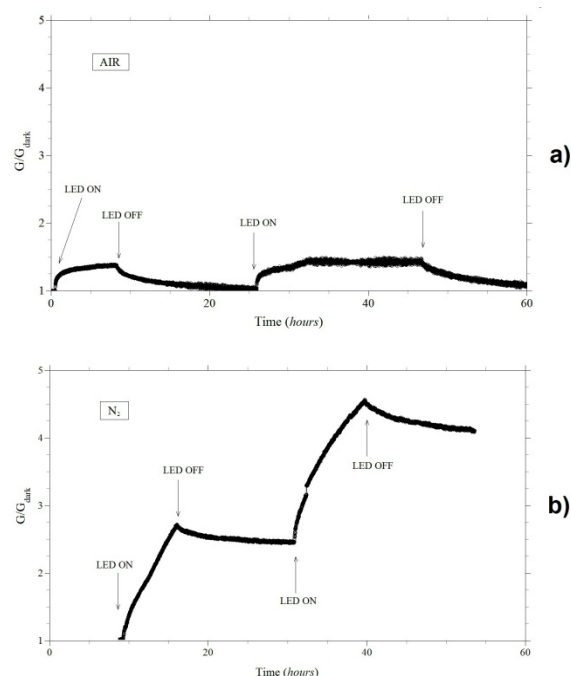


Fig. 3. Ratio between the instantaneous conductance of the sensor and its value in dark at the beginning of the measurement, during light-dark cycles. a) In air, b) in nitrogen.

Three main things should be noticed:

- in nitrogen the relative increase in conductance after switching on the LED is much stronger than in air;
- in air the increase in conductance is reversible, while in nitrogen, after the switching off of the LED, the conductance hardly departs from the value reached in light;
- the conductance change in both environments is very slow (many hours).

These facts are in contrast with what one would expect from a single semiconductor crystal. Indeed, the energy of the impinging photons, corresponding to a wavelength of 400 nm, is 3.1 eV, which is greater than the energy gap of the material, 2.56 eV. Thus, the change in conductance after illumination of the surface is expected to depend mainly on interband electronic transitions. If this were the case, the conductance would change very rapidly after illumination/darkening, while the obtained data seem to obey to timescales typical for chemical processes at low temperatures. Moreover, (a) and (b) lead to think to a direct action of the photons on the adsorbed oxygen atoms/molecules. In particular, they are in agreement with the assumption that the photons force the desorption of the surface adsorbed oxygen. Indeed, in air, the weaker increase of conductance after illumination is supposed to depend on the achievement of a new equilibrium between the desorption/adsorption of oxygen, whereas in nitrogen this equilibrium cannot be achieved due to the absence of oxygen. As a consequence, in nitrogen the removed surface oxygen is hardly replaced, therefore the conductance increases until there are ions to remove. Moreover, in air, the conductance value after darkening can return to its previous value because the atmospheric oxygen allows the re-adsorption, whereas in nitrogen it cannot, due to absence of oxygen.

The light-induced oxygen desorption can occur following two different routes:

- 1) the impinging photon stimulates the creation of an electron-hole pair inside the material; if it is close enough to the surface, the electric field could move the hole toward the surface, and it can recombine with an electron trapped in a surface state, causing the desorption of an oxygen atom;
- 2) the impinging photon are directly absorbed by the surface oxygen, causing its desorption and releasing the trapped electron to the material.

These two routes are both allowed because the adsorption energy of an oxygen atom on a metal oxide surface is of the order of 1.50 eV [7], thus the impinging UV photons have enough energy to force the desorption of surface oxygen atoms.

Conclusions

The effect of the surface illumination on the conductance of a WO_3 gas sensor has been investigated. Measurements have been carried out in dry air and in nitrogen with the help of a UV LED and a chamber provided with a transparent window and an optical system. The observed behavior suggests a strong contribution of surface processes to the conductance change after illumination/darkening. A simple model based on a light-induced oxygen desorption process was proposed.

Acknowledgements

This work was supported by Programma Operativo FESR 2007-2013 della Regione Emilia-Romagna – Attività I.1.1.

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