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Photo-activation of cadmium sulfide films for gas sensing

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Abstract

Photo-activation of semiconductor films for room temperature gas sensing is a research topic intensely studied during the last years. Even though the most investigated semiconductors in the field of conductometric gas sensors are metal oxides, cadmium sulfide shows very interesting photo-stimulated properties, in particular it shows chemoresistivity that can be activated by light at room temperature. In this work, the photo-enhanced sensing properties of CdS films toward five target gases are studied as a function of the wavelength of the impinging radiation. It resulted that the chemical activity of CdS at surface is strongly dependent on the exciting wavelength. The peak of the response was found for the wavelength equivalent to the bandgap energy, this meaning a bandgap-resonant behavior of the surface chemical activity that can possibly be employed for gas sensing applications.

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Keywords: Cadmium sulfide; Photo-activation; Photoconductance; Room temperature gas sensing

1. Introduction

Conductometric gas sensors are traditionally based on thin or thick films of polycrystalline metal oxides, such as tin dioxide, titanium dioxide, zinc oxide, tungsten trioxide, etc. with dopants and/or in mixed solutions [1-6]. These

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oxides are all wide gap semiconductors which show chemoresistivity due to the presence of electronic surface states, on which the sensing mechanism is based. Gas-surface chemical reactions provide charge transfer in these states, modulating the electrostatic potential barrier at the surface of the grains of the sensing material, and, as a consequence, the electrical resistance of the film [3,7]. Since the barrier height depends on the Fermi level position with respect to the conduction band minimum, which is determined by gas-surface interaction, we expect that the sensing principle does not depend on whether the material is an oxide or not. Therefore, contrary to what is found in the literature, there is no formal reason to restrict the research on oxides only.

Cadmium sulfide (CdS) is an inorganic semiconductor with a bandgap of 2.40 eV, predominantly used as pigment, but it is widely employed in several areas of science and technology due to its valuable properties, such as piezoelectricity, photoconductivity, electroluminescence and more [8-11]. CdS-based technology has multiple applications, e.g. solar cells, photoresistors, transistors and piezoelectric transducers working in very high frequency ranges. Besides these well-consolidated applications, CdS shows also chemoresistivity [12], but this valuable property was scarcely investigated by the scientific community. As a confirmation, very little can be found in literature about CdS as gas sensing material. Particularly interesting is the fact that, as for other semiconductors which show both photoresistivity and chemoresistivity, such as ZnO and WO_3 [13-15], CdS chemoresistivity can be activated by light at room temperature. This interesting property allows the realization of gas sensors that do not require any kind of heating to operate. Electromagnetic irradiation promotes electrons into the conduction band, increasing film's conductivity and controlling surface chemistry [16].

2. Synthesis, experimental procedures and characterizations

CdS nanopowder was synthesized in water, at room temperature and atmospheric pressure by a simple precipitation route. A solution of cadmium acetate hydrate, as precursor for cadmium, and o-diaminobenzene in water, was prepared and stirred for two hours. Then, a proper quantity of thioacetamide, as sulfur precursor, was added to the solution and the mixture was stirred again for several hours. The resulting yellow-orange precipitate was vacuum-filtrated and washed several times with water and methanol. The drying of the product was performed by heating in oven for 4 hours at 40°C.

The obtained CdS powder was characterized by means of X-Ray power Diffraction, SEM imaging and TG/DTG thermal analysis. It resulted that the material was crystalline, being hawleyite the only crystal phase, with nanosized grains of spherical morphology. A SEM image is showed in Fig. 1. Thermal analysis revealed a good thermal stability of the obtained material up to 500°C.

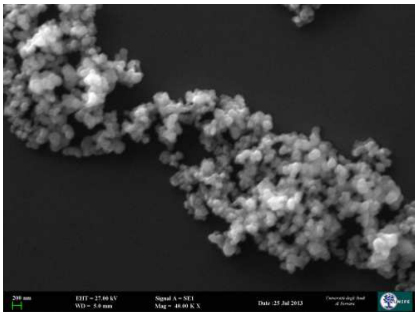

Fig. 1. SEM image of the obtained CdS powder.

The sensing films were realized by means of screen-printing technique, depositing the synthesized material onto alumina substrates with pre-deposited electrical contacts. To obtain a screen-printing paste with the suitable rheological properties, a proper amount of organic vehicles had to be added to the CdS powder. After the deposition, the films were subjected to thermal stabilization in a muffle oven in air, for 12 hours at 180°C, to stimulate the evaporation of organic vehicles. Then, the device was mounted on a suitable support to be interfaced with the electronic measuring system.

To perform the gas measurements, the CdS sensors were positioned in a test chamber, equipped with a glass window, controlling the composition of the inside atmosphere with the flow-through technique. Monochromatic illumination was provided by the light produced by a LED, focused on the film through the glass window by means of an optical system. To investigate on the effect of irradiation energy, we used five different wavelengths: 400 nm (violet), 468 nm (blue), 525 nm (green), 592 nm (yellow) and 645 nm (red). The electrical conductance of the films was constantly monitored during gas measurements by means of proper electronics interfaced to a data-acquiring system. The tested gases, with their relative concentrations, were CO (10 ppm), CH_4 (2500 ppm), H_2S (10 ppm), ethanol (10 ppm) and benzene (10 ppm). Each gas concentration was flowed for 15 minutes before restoring the air flow.

3. Sensors performance

As a consequence of the electro-optical properties of CdS, illumination of the films resulted in an increase of the electrical conductivity which depended on the energy of the impinging radiation. According to the firsts works on CdS [17], we found the maximum photoconductance for the green light at 525 nm (2.37 eV), which corresponds to the bandgap energy of the material. After switching on the LED, we waited for a few hours to stabilize the photoconductance of the film, then we injected the target gases in the test chamber.

The response of a sensor to a specific gas concentration was defined as

$$R = \frac{G_{gas} - G_{air}}{G_{air}} \tag{1}$$

where G_{gas} and G_{air} are the electrical conductance in gas and in air, respectively. The definition in Eq. (1) implies that R is zero for a gas concentration which does not cause any change in the electrical conductance of the film. The response was found to depend on the illumination wavelength. A plot of the response of a CdS film vs. time, during the injection of 2500 ppm of methane with different illumination wavelengths, is reported in Fig. 2a, being the time behavior for the other gases very similar to this one.

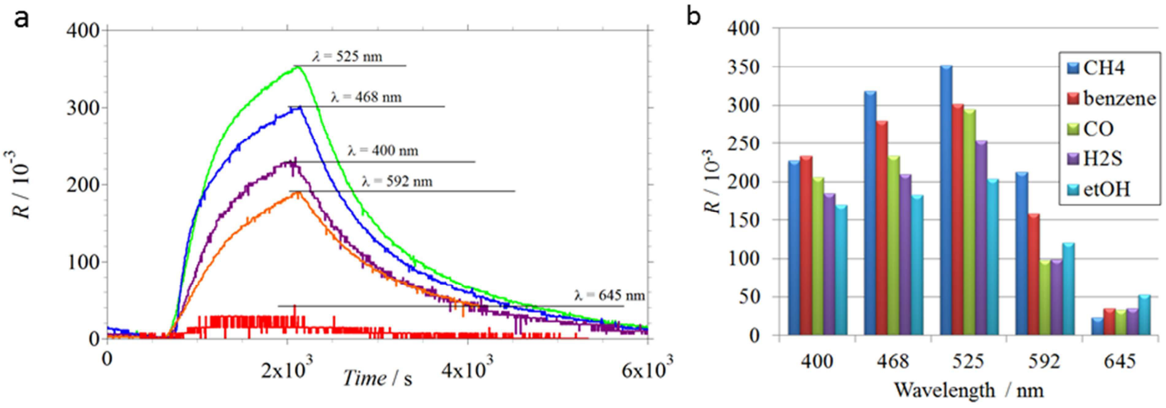

Fig. 2. (a) response vs. time of a CdS sensor before, during and after the injection of 2500 ppm of methane. The five curves correspond to the five wavelengths of the impinging radiation; (b) responses to the tested gases as a function of the exciting wavelength.

The response of a CdS sensor to the tested gases, after 15 minutes of exposure, is reported in Fig. 2b, for each illumination wavelength. As can be noticed, the response to whatever gas is wavelength-dependent, in particular the maximum of the response was found for the green light (525 nm), as for the maximum of the photoconductance.

This observation is worth attention, because it means that, not only the photoconductance is bandgap-resonant, but also the photo-enhanced surface chemistry, which is responsible for the conductance changes in chemoresistive sensors. A deeper discussion of these phenomena and the possible mechanisms can be found in [16].

4. Conclusions

Nanosized CdS powder was synthesized with a simple route and characterized from the structural, morphological and thermal point of view, proving to be monophasic CdS (crystal phase was hawleyite) with spherical grains and good thermal stability up to 500°C. Conductometric gas sensors, based on screen-printed films of the obtained CdS, were realized and tested at room temperature under electromagnetic radiation. Tests were performed with CH_4, benzene, CO, H_2S and ethanol with different radiation wavelengths, ranging from violet to red. The best response for each gas was recorded for the green light, which corresponds to the bandgap energy of the semiconductor. This result extends the resonance with the bandgap energy, already known for the photoconductance, to the surface chemistry. The present work proves the possibility to use polycrystalline CdS for room temperature gas sensing, expanding also the information about the properties of this material when used as heterogeneous photocatalyst.

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References

[1] R. Mishra, K. Rajanna, Metal-oxide thin film with Pd, Au andAg nanoparticles for gas sensing applications, Sensor Mater. 17 (2005) 433-440.

[2] R.A. Kadir, R.A. Rani, A.S. Zoolfakar, J.Z. Ou, M. Shafiei, W. Wlodarky, K. Kalantar-Zadeh, Nb_2O_5 Schottky based ethanol vapour sensors: Effect of metallic catalysts, Sens. Actuators B 202 (2014) 74-82.

[3] M.C. Carotta, M. Benetti, E. Ferrari, A. Giberti, C. Malagù, M. Nagliati, B. Vendemiati, G. Martinelli, Basic interpretation of thick film gas sensors for atmospheric application, Sens. Actuators B 126 (2007) 672-677.

[4] M.C. Carotta, A. Cervi, A. Giberti, V. Guidi, C. Malagù, G. Martinelli, D. Puzzovio, Metal-oxide solid solutions for light alkane sensing, Sens. Actuators B 133 (2008) 516-520.

[5] A. Giberti, M.C. Carotta, B. Fabbri, S. Gherardi, V. Guidi, C. Malagù, High-sensitivity detection of acetaldehyde, Sens. Actuators B 174 (2012) 402-405.

[6] Y.-C. Liang, W.-K. Liao, X.-S. Deng, Synthesis and substantially enhanced gas sensitivity of homogeneously nanoscale Pd- and Au-particle decorated ZnO nanostructures, J. Alloy Compd. 599 (2014) 87-92.

[7] C. Malagù, M.C. Carotta, A. Giberti, V. Guidi, G. Martinelli, M.A. Ponce, M.S. Castro, C. M. Aldao, Two mechanisms of conduction in polycrystalline SnO_2, Sens. Actuators B 136 (2009) 230-234.

[8] D. Shvydka, J. Drayton, A.D. Compaan, V.G. Karpov, Piezo-effect and physics of CdS-based thin film photovoltaics, Appl. Phys. Lett. 87 (2005) 123505.

[9] S.-L. Fu, T.-S. Wu, M.-P. Houng, The photoconduction mechanisms of screen-printed CdS films, Sol. Energ. Mater. 12 (1985) 309-317.

[10] I.J. Ferrer, P. Salvador, Photoluminescence and electroluminescence mechanisms at polycrystalline CdS in air and in contact with aqueous electrolytes, J. Appl. Phys. 66 (1989) 2568.

[11] R.R. Arya, P.M. Sarro, J.J. Loferski, Efficient cadmium sulfide on silicon solar cells, Appl. Phys. Lett. 41 (1982) 355.

[12] V. Golovanov, V. Smyntyna, G. Mattogno, S. Kaciulis, V. Lantto, Oxygen interaction od CdS-nased gas sensors with different stoichiometric composition, Sens. Actuators B 26 (1995) 108-112.

[13] C. Malagù, M.C. Carotta, E. Comini, G. Faglia, A. Giberti, V. Guidi, T.G.G. Maffeis, G. Martinelli, G. Sberveglieri, S.P. Wilks, Photo-induced unpinning of Fermi level in WO_3, Sensors 5 (2005) 594-603.

[14] M.C. Carotta, A. Cervi, A. Fioravanti, S. Gherardi, A. Giberti, B. Vendemiati, D. Vincenzi, M. Sacerdoti, A novel ozone detection at room temperature through UV-LED-assisted ZnO thick film sensors, Thin Solid Films 520 (2011) 939-946.

[15] A. Giberti, C. Malagù, V. Guidi, WO_3 sensing properties enhanced by UV illumination: An evidence of surface effect, Sens. Actuators B 165 (2012) 59-61.

[16] A. Giberti, B. Fabbri, A. Gaiardo, V. Guidi, C. Malagù, Resonant photoactivation of cadmium sulfide and its effect on the surface chemical activity, Appl. Phys. Lett. 104 (2014) 222102.

[17] G. Kuwabara, The optical and electrical properties of cadmium sulfide films, J. Phys. Soc. Jpn. 9 (1954) 97-102.