Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 168 (2016) 276 – 279

Procedia Engineering

www.elsevier.com/locate/procedia

30th Eurosensors Conference, EUROSENSORS 2016

Chemoresistive gas sensor based on SiC thick film: possible distinctive sensing properties between H_2S and SO_2

A. Gaiardo[a,b,*], P. Bellutti[b], B. Fabbri[a], S. Gherardi[a], A. Giberti[c], V. Guidi[a], N. Landini[a], C. Malagù[a], G. Pepponi[b], M. Valt[b], G. Zonta[a]

[a] *Department of Physics and Earth Sciences, University of Ferrara, Via Saragat 1/c, 44122 Ferrara, Italy*
[b] *MNF - Micro Nano Facility, Bruno Kessler Foundation, Via Sommarive 18, 38123 Trento, Italy*
[c] *S.r.l., Mist-er, Via P. Gobetti 101, 40129 Bologna, Italy*

Abstract

Commercially available nanosized powder of silicon carbide (named SiC), was thermally, morphologically and structurally characterized. After that, it was screen-printed onto alumina substrates in order to obtain thick films to be tested as functional material for conductometric gas sensors. Samples were exposed to SO_2 and H_2S, gases with high importance in many application fields, with the aim of verifying its capability of distinguishing between them. The characterization highlighted that this semiconductor type is selective for sulphur dioxide (SO_2), in concentrations within the ppm range. This interesting result was found at high temperatures (600-800°C), useful for harsh environmental, and the measurements proved to be completely free from humidity interference. Applications of such a sensor could span many fields, since SO_2 plays an important role in air pollution, industrial processes and wine making monitoring.

Peer-review under responsibility of the organizing committee of the 30th Eurosensors Conference

Keywords: Gas Sensor; Silicon Carbide; SiC; Thick Film; SO_2; High Selectivity

---

1. Introduction

Silicon carbide (SiC) is a long-time known material, massively produced since 1890, which shows interesting mechanical properties. Ceramics obtained by sintering SiC grains are very hard and can be employed in diverse sectors e.g., in the construction of car brakes, of bullet-proof vests and in general for high endurance applications [1]. A peculiarity of SiC is also its extraordinary thermal strength, holding stability even above 1000°C. This characteristic makes SiC suitable for high temperature applications (SiC melting point is above 3000 K at 35 atm) [2]. As regards to the electrical properties, this material is a semiconductor with a mid-high band-gap, i.e., in the 2.3-

Peer-review under responsibility of the organizing committee of the 30th Eurosensors Conference
doi:10.1016/j.proeng.2016.11.191

3.3 eV range, depending on the crystal phase [3]. The main electronic applications of SiC are light-emitting diodes and hi-temperature and/or hi-voltage devices, as JFETs and MOSFETs rated at 1200 V [4].

However, silicon carbide is also a material that can be synthesized in the form of nanostructured particles [5]. Nanostructured semiconductors show very different electrical properties compared to single crystals, due to the major role that the surface potential plays in the conductive mechanism. Indeed, under proper operating conditions (thermo-activation or photo-activation modes), a nanostructured material can show a surface reactivity high enough to dominate the resistance of the whole nanostructure [6]. In particular, chemoresistive gas sensors take advantage of this phenomenon, transducing the variations of the environmental chemical composition into electrical resistance variations of a film made with the nanostructured material. Silicon carbide results so widely studied, in the field of gas sensing technology, as a substrate of sensor devices [7]. In this work we investigated on silicon carbide chemoresistive properties, encouraged by the wide range of fields in which SiC can be employed and by the possibility to produce it in the form of a nanosized powder. Indeed, through the combination of high stability and surface reactivity, it is possible to obtain a gas sensor device suitable to commercial use. For this purpose, a commercially available SiC nanosized powder was purified through washing and heat treatment at high temperature. Then, the sample was characterized from the morphological, thermal and structural point of view. Afterwards, the SiC powder was screen-printed onto an alumina substrate. The thick film obtained was tested as sensing layer for gas sensors, by exposing the SiC film in particular to H_2S and SO_2, because it is important for industrial application to have a sensor capable of distinguishing between these two chemical species [8]. At the same time, these gases are the two principal products of volcanic activity [9]. With this aim, sensor responses were investigated at operating temperatures ranging from 250°C to 750°C. The most interesting result was that SiC sensors showed a selectivity response to sulphur dioxide in the concentration range of some ppm, in dry condition. Moreover, the electrical characterization with the tested gases showed an increase of the response to SO_2 in humidity condition. This result was found for quite high working temperatures (600°C and higher), that suggest a potential use of this sensing material also in harsh environment.

Nomenclature

SiC	Silicon Carbide

---

* Corresponding author. Tel.: +39 0532 974294; fax: +39 0532 974211.
E-mail address: grdndr@unife.it

2. Experimental section

Commercial Silicon Carbide nanopowder, with average size of 50 nm, was treated in order to reduce the grain size and purified the sample. With this purpose SiC was crumbled with a Retch MM200 bull mill, at high rpm, for several hours. After that, the sample was washed several time with alcohols and water by means centrifuge method. Finally, the SiC powder was heat treated at 900°C for two hours, in order to purify the sample from possible other chemical residue.

2.1. Structural, Morphological and Chemical Characterization

X-Ray Diffraction (XRD) analysis, reported in Fig. 1, was carried out by using a Bruker D8 Advance diffractometer with an X-ray tube operating at 40 kV and 40 mA, and equipped with a Si (Li) solid-state detector (SOL-X) set to measure CuKα 1.2 radiation [10]. As it can be seen, the data elaboration with TOPAS software highlighted the presence of three different crystal phases in the SiC sample. The average size of nanograins was about 30 nanometer. This experimental data showed that the bull mill treatment produced a decrease of the average grain size.

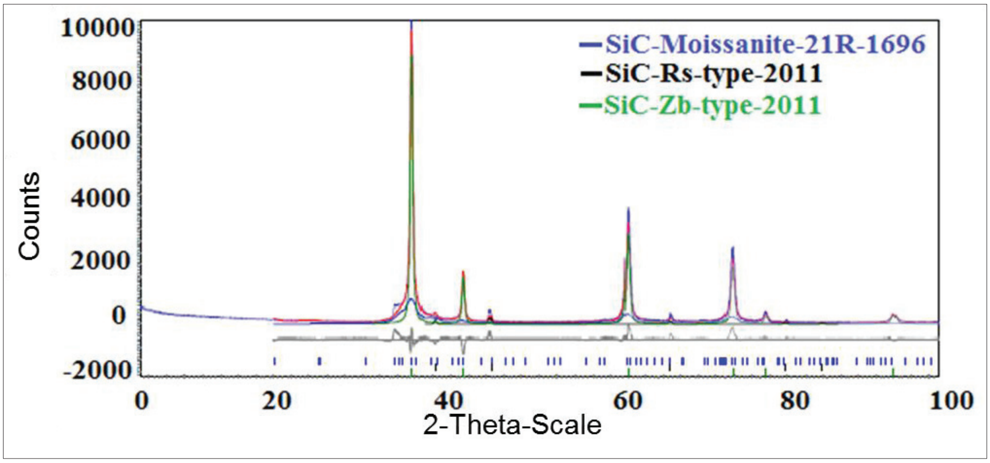

Fig. 1: X-ray Diffraction analysis of the treated SiC nanopowder

In the Fig. 2a, as inset, is reported the EDX chemical characterization of SiC sample. The analysis highlighted the high chemical purity of the treated powder. In Figs. 2a and 2b are shown images obtained by means scanning electron microscopy and transmission electron microscopy. From these arose that the morphology of SiC powder is regular and the SiC sample is composed by nanograins.

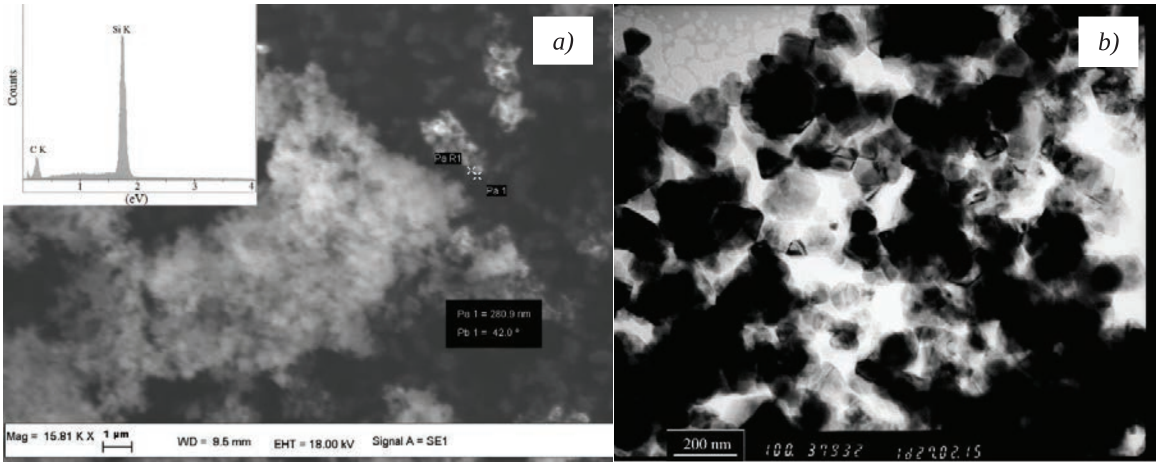

Fig. 2: a) Electron Scan Microscopy image of the treated SiC nanopowder. Inset: EDX analysis of the sample.
b) Transmission Electron Microscopy image of the SiC sample

2.2 Electrical Characterization

SiC thick film were screen printed onto alumina substrate starting from treated SiC powder with the addition of organic vehicles [11]. The devices obtained were electrical characterized in a test chamber by means of the flow-through technique [12]. Sensor responses were investigated at working temperatures ranging from 250°C to 650°C. The concentration of H_2S and SO_2 were chosen following Threshold Limit Value.

Measurements highlighted that SiC sensors remained insensitive to the two gases up to 600°C, in dry air. At this temperature, the layers showed a response only to 10 ppm of SO_2. The response to SO_2, calculated as the conductance ratio between the signal obtained with the target gas and the signal in air, increased at a working temperature of 650°C. Instead, no change in the conductance value was recorded with 10 ppm of H_2S for both temperatures, as it can be seen in Fig. 3a.

Afterwards, SiC films response to 10 ppm of SO_2 were tested in humidity condition. As it can be seen in Fig. 3b, the sensor response to 10 ppm of SO_2 increased in the presence of 50% of relative humidity.

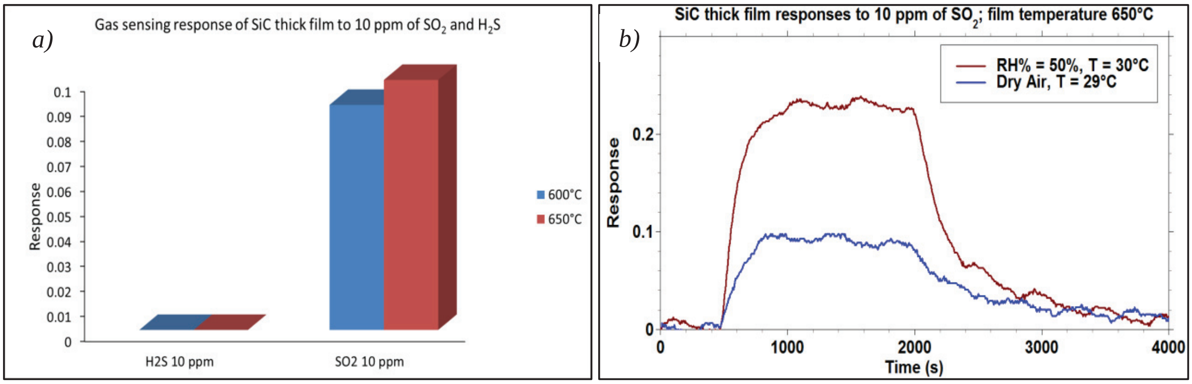

Fig. 3: a) Gas sensing response of SiC thick films to 10 ppm of H_2S and 10 ppm of SO_2, respectively, at working temperature of 650°C and 700°C, in dry air.

Conclusions

This work was a feasibility study for the realization of a gas-sensing device based on silicon carbide commercial powder and results were highly encouraging. The sensing characterization of SiC thick films showed that it can be employed in the discrimination between SO_2 and H_2S (in concentrations up to the ppm level), at high temperature (600°C and higher) and in dry air conditions. The sensor response to SO_2 and its selectivity to this gas was in wet air environment, highlighting a possible application of SiC in the detection of this toxic gas in harsh environments.

Acknowledgements

Thanks to Daniela Palmeri of the Ferrara Centre of Microscopy.

References

[1] Z. Li et al., International Journal of Applied Ceramic Technology, article in press, doi: 10.1111/ijac.12514

[2] S. Cao et al., Journal of Materials Science, 51, pp. 1-10 (2016); doi: 10.1007/s10853-016- 9780-3

[3] N. Alaal et al., Journal of Physics D: Applied Physics, vol. 49, issue 8 (2016); doi: 10.1088/0022-3727/49/10/105306

[4] R. Elpelt et al., Materials Science Forum, ICSCRM 2015, Volume 858, 2016, Pages 817-820, doi: 10.4028/www.scientific.net/MSF.858.817

[5] C. Su et al., Journal of Macromolecular Science, Part B: Physics, Volume 55, Issue 6, 2 June 2016, Pages 627-641, doi: 10.1080/00222348.2016.1179248

[6] Guidi et al., Materials Science and Applications in Sensors, Electronics and Photonics, ISBN: 978-1-84569-988-8

[7] M. Kachniarz et al., Advances in Intelligent Systems and Computing, Volume 352, 2015, Pages 111-120, doi: 10.1007/978-3-319-15835-8_13

[8] J.F.D.S. Petruci, Analytical Chemistry, Volume 87, Issue 19, 15 September 2015, Pages 9605-9611, doi: 10.1021/acs.analchem.5b02730

[9] Henley et al., Journal of Volcanology and Geothermal Research, Volume 324, 15 September 2016, Pages 190-199, doi: 10.1016/j.jvolgeores.2016.04.024

[10] A. Giberti et al. Sensors and Actuators, B: Chemical, 223, pp. 827-833, (2016), doi: 10.1016/j.snb.2015.10.007

[11] A. Gaiardo et al. Proceedings of the 2015 18th AISEM Annual Conference, AISEM 2015, (2015), doi: 10.1109/AISEM.2015.7066860

[12] A. Gaiardo et al. Sensors (Switzerland), 16 (3), (2016), doi: 10.3390/s16030296