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Gas sensing by thermoelectric voltage fluctuations in SnO_2 nanoparticle films

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Abstract

Experimental results of gas sensing by thermoelectric voltage fluctuation measurements in gas sensors are presented. The applied sensors consist of monodispersed SnO_2 nanoparticles films, with a mean diameter of 20 nm. The voltage fluctuations in the sensor films were observed with and without external voltage bias and its power density spectrum exceeded at least a thousand times its thermal noise. The power density spectrum of the observed stochastic signal changed in different gases by a factor of three while the change of the sensor resistance was only 2–3%. The stochastic signal observed in the sensor without external voltage bias is caused by the temperature gradient in the film. The results show that thermoelectric fluctuations, without external voltage bias, can be applied for use in gas sensing.

Keywords: Fluctuation-enhanced sensing; Nanoparticles; Stochastic processes; Bias-free Taguchi sensor

1. Introduction

It has been known [1] for a long time that the processes of gas adsorption on porous semiconductor surfaces can change the electrical properties of the surface. Taguchi gas sensors are based on grainy metal-oxide semiconductor films (e.g. SnO_2) with transport properties that are very sensitive to variations of the composition of the ambient gas. Usually, the DC resistance is measured and used for gas sensing in many practical applications [2]. Significantly greater sensitivity (DC resistance change) has been observed with smaller grain sizes, even at lower substrate temperatures [3]. Presently, most artificial noses need an array of different sensors in order to analyze gas mixtures [4] because each sensor provides only one component (point) of a pattern which is needed for gas recognition. This fact implies a variety of practical problems that limit their practical applications. For example, the power consumption, and the strong need and high cost of sensor maintenance are among the most significant problems. Promising results have been observed when the fluctuations of the gas-sensitive film are applied for sensing [5,6]. Then, the statistical measures of the fluctuations provide the required pattern, thus a single sensor can be used as a complete electronic nose detecting complex mixtures [6].

2. Description of the sensors

The gas sensors were prepared from monodispersed SnO_2 nanoparticles with a mean particle diameter of 20 nm [7]. The gas-sensitive film consists of a particle size of about 20 nm. The structure of the sensors is presented in Fig. 1 (top view)

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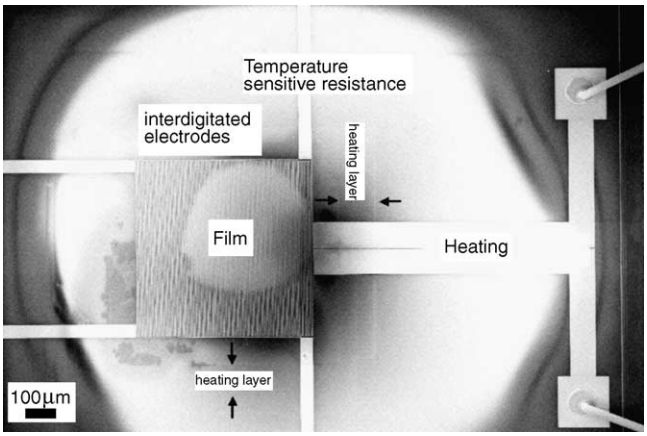

Fig. 1. Micrograph of the gas sensor structure (top view).

and Fig. 2 (side view). The gas-sensitive film is deposited on the surface of an interdigitated structure of metal electrodes by means of low-pressure impaction [3]. The 1 mm^2 structure consists of 160 interdigitated fingers (each ∼1 mm long) with a width of 2 μm and an identical separation. The electrodes are implanted in phosphor-doped silicate glass (PSG). This ensures a more homogenous nanoparticle film deposition [8]. The electrode structure is enclosed by a heater which is embedded in the PSG. A poly-Si layer serves as a heater element and is mounted on a low-pressure (LP) nitride. The gas-sensitive film is situated asymmetrically to the heater layer. A temperature sensitive resistor is situated close to the interdigitated electrodes. This resistance allows the measurement of the temperature of the substrate surface.

3. Experimental results

DC resistance and voltage fluctuation measurements were performed to test the sensing properties of the SnO_2 nanoparticle sensor. The sensor was placed in a stainless steel gas chamber of 1 dm^3 volume and exposed to synthetic air, ethanol (300 ppm) and hydrogen (1000 ppm), both diluted in synthetic air. The constant flow of the applied gases did not exceed 0.2 l/min in order to minimize possible gas turbulence effects. The microscopic voltage fluctuations across the gas sensor were amplified and filtered by a Stanford SR560 preamplifier and were recorded and analyzed by a data acquisition unit (PowerLab/4SP, ADInstruments). The power density spectrum was determined via fast Fourier transformation using the Welch method [9]. The gas sensor was biased by different voltages starting from 0 up to 1.6 V. The voltage fluctuations of the sensor exposed to ethanol or hydrogen stabilized and became stationary after 7 h (ethanol) and 2 h (hydrogen), respectively. This slow stabilization after gas exposure is due to the relatively low temperature of the sensor $T = 150\,^{\circ}$C, which was limited by the present technology and the required long lifetime. Work is proceeding to develop sensors that can tolerate higher temperatures.

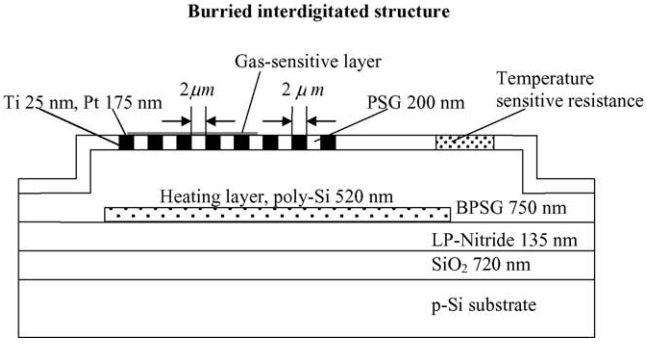

Fig. 2. A schematic view of the gas sensor structure (side view).

In all figures where we show spectra, we multiplied the power density spectrum $S(f)$ by the frequency f, which is a common fashion when plotting $1/f$ like spectra, like ours. This makes small changes in the shape easier to observe. Fig. 3 shows a typical response of the sensor, with zero external voltage bias, after the voltage fluctuations become stationary. The observed power density spectrum was at least a thousand times greater than the thermal noise of the sensor resistance R_S at this temperature. A small thermoelectric voltage, of the order of millivolts, between the electrodes was observed due to temperature gradients in the sensor film and a temperature difference between the electrodes.

In different gases, the fluctuations varied by a factor of three while variations of the sensor resistance remained within 3%. The pattern of the spectrum depended on the ambient gas in a unique way, see Fig. 4. It is obvious from these facts that the spectrum provides significant more sensing information than the simple resistance of the sensor. With increasing temperature, the intensity of the spectrum increased progressively as shown in Fig. 5. Fig. 6 shows a typical time evolution of the response of the sensor exposed to ethanol. When the exposition to ethanol was complete, the

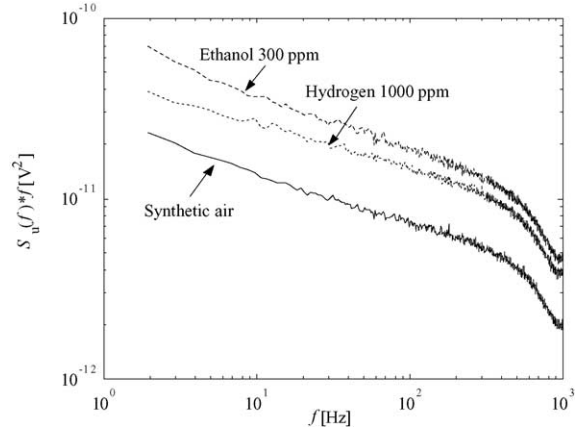

Fig. 3. Power density spectrum multiplied by frequency f, for the sensor exposed to synthetic air, ethanol (300 ppm), hydrogen (1000 ppm); sensor temperature 150 °C. Resistance was about $R_S = 510\,\Omega$.

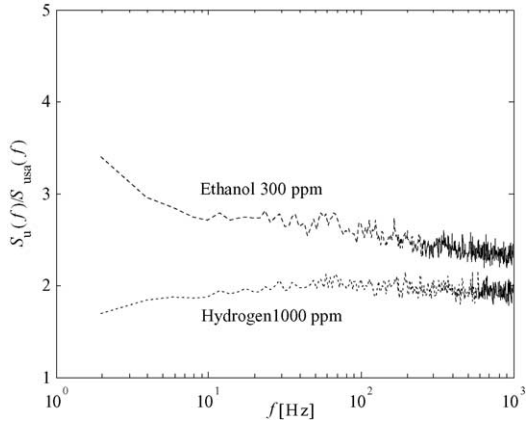

Fig. 4. Relative changes of power density spectrum $S_u(f)$ to the spectrum $S_{usa}(f)$ estimated for the sensor exposed to the synthetic air vs. frequency f; sensor temperature 150 °C.

spectrum gradually returned to the original level. This indicates the total recovery of the sensor surface after the ethanol exposure.

The situation with hydrogen was very different (Fig. 7). The stabilization time of the sensor did not exceed 2 h. However, the sensors developed a strong memory as a result of exposure to hydrogen. Even several days after finishing the exposure to hydrogen, the spectrum stayed at the newly acquired level. The slope of the spectrum in a log–log plot around −1.5, in the high-frequency limit, which suggests the presence of a diffusion noise process [11,12] caused by hydrogen diffusing through the film between the electrode fingers. When, at non-zero bias, the voltage across the sensor exceeded 0.1 V the spectrum started to increase and changed its shape. This is an indication of drift related changes as a result of the diffusive fluctuation dynamics.

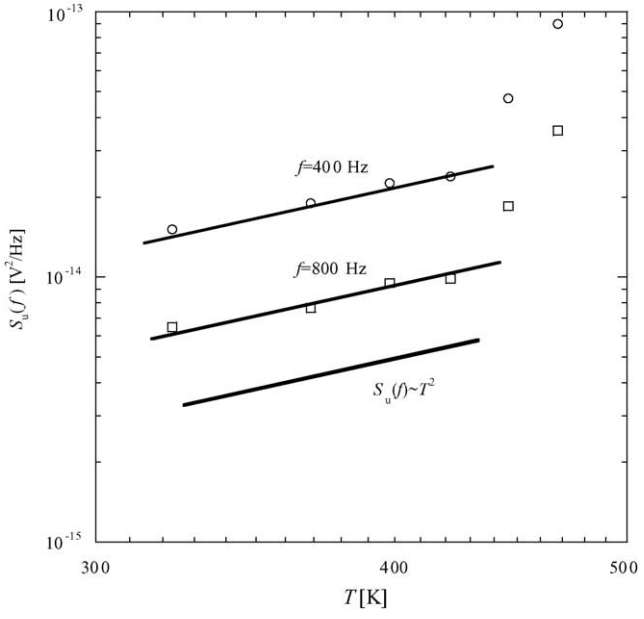

Fig. 5. Changes of power density spectrum $S_u(f)$ vs. temperature T, for the sensor exposed to synthetic air after finishing burn in process.

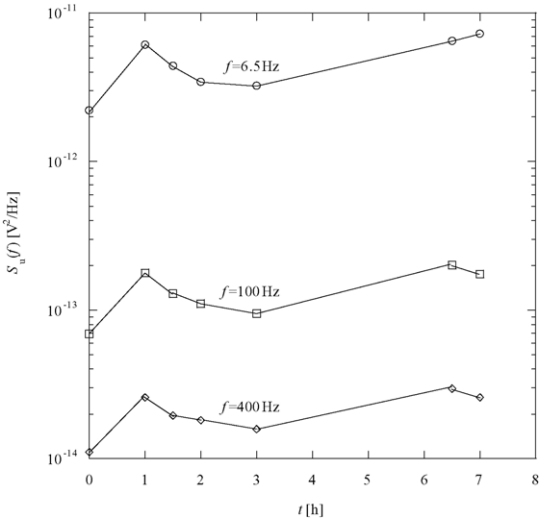

Fig. 6. Changes of voltage noise spectrum after sensor exposing to ethanol (300 ppm); sensor temperature 150 °C, gas flow started 6 h before first noise registration at t = 0.

4. Discussion

The observed fluctuations do not change their intensity and dynamics when the DC voltage across the sensor is lower than 100 mV. At zero voltage bias, the resistance fluctuations of the nanoparticle film cannot generate the observed voltage fluctuations because of Ohm's law. This fact and the strong dependence of the observed stochastic signal on the sensor temperature (Fig. 5) suggest that the voltage fluctuations in this regime are generated by processes which are sensitive to the temperature and temperature dif-

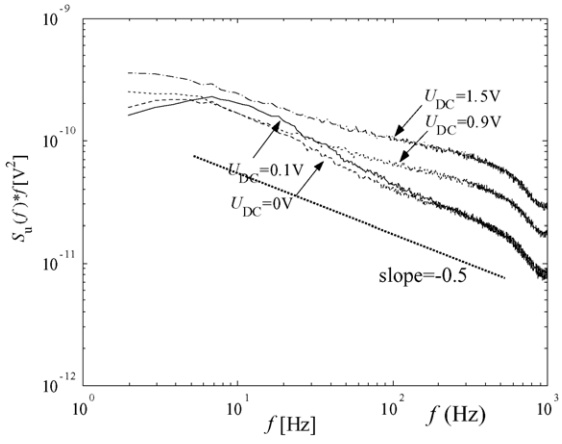

Fig. 7. Sensor exposed to synthetic air after being exposed to hydrogen (1000 ppm) at sensor temperature 150 °C. The dashed line with slope −0.5 corresponds to a spectral slope of −1.5 which is the signature of a defect diffusion noise process.

ferences within the sensor structure. The detailed analysis of the sensor structure makes it plausible to suppose an inhomogeneous temperature distribution in the nanoparticle film:

- The heating layer is located asymmetrically below the interdigitated electrode structure;
- The heating layer is located asymmetrically below the gas-sensitive layer.

Both facts can contribute to temperature inhomogeneities across the junctions formed by the metal electrodes and the nanoparticle film. The thermoelectric voltage is proportional to the temperature gradient ΔT which is roughly proportional to the difference of the sensor temperature and the ambient temperature [10]. The work function of the electrode–film junctions is modulated by the local concentration of diffusing fragments of absorbed gases which results in a fluctuation of the thermoelectric voltage. The change of the power density spectrum at a given frequency is due to two separate factors. First, the amplitude of the induced thermoelectric voltage fluctuations is roughly proportional to the temperature gradient. Second, the diffusion of the defects is a thermally activated process which means a temperature dependence in the speed of the fluctuations. The two effects, at a given frequency, cause a well-defined temperature dependence of the spectrum (Fig. 5). The geometrical aspect of the proposed mechanism can explain the spectra of voltage fluctuations of the sensor after it is exposed to hydrogen. A diffusion noise spectrum, with slope around −1.5 in log–log plot in the high-frequency limit, is shown in Fig. 7. Due to the multiplication by the frequency, the dashed line with slope −0.5 corresponds to a spectral slope of −1.5. The crossover frequency $f_c \approx 6$ Hz, where the slope changes, indicates a geometrical crossover where the diffusion process reaches through the junction region during the time given by reciprocal frequency [12,13]. The characteristic length L of the junction region has to satisfy $L < 2$ μm because of the distance between the electrode fingers, see Section 2. This implies that the diffusion coefficient of fragments $D = \pi f_c L^2 < 7.5 \times 10^{-7}$ cm^2/s. The shape of the spectrum did not indicate a clear diffusion noise mechanism with a single type of diffusor when the sensor was exposed to ethanol. One explanation is that the ethanol molecules probably broke into fragments of various sizes with a range of diffusion coefficients and crossover frequencies. In the voltage range $U_{DC} > 100$ mV the fluctuations get dominated by the resistance fluctuations (conductance noise) in the film (Fig. 8). The voltage spectrum density becomes proportional to the square of the applied DC voltage $S_u(f) \sim U_{DC}^2$ when $U_{DC} \geq 0.1$ V.

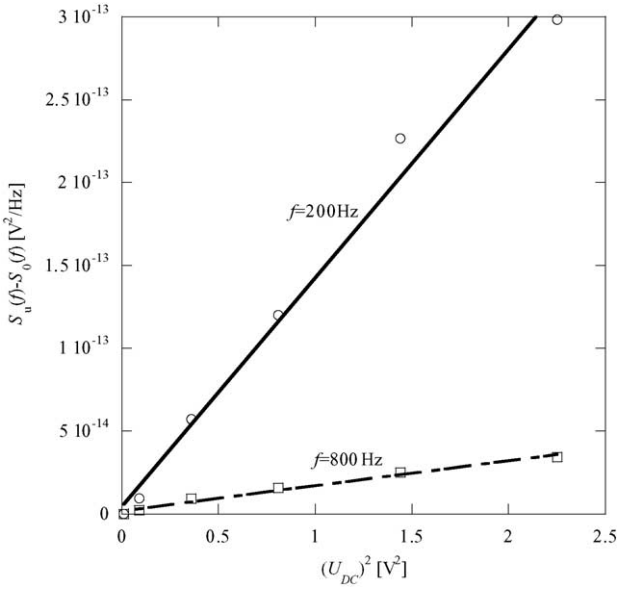

Fig. 8. Changes of power density spectrum $S_u(f)$ of sensor exposed to synthetic air after being exposed to hydrogen (1000 ppm) vs. U_{DC} voltage applied across sensor; sensor temperature 150 °C, $S_0(f)$-voltage spectrum density at $U_{DC} = 0.1$ V.

5. Conclusion

The observed fluctuations without bias voltage are very intensive and are generated by non-homogenous temperature distribution. This thermoelectric effect suggests a new family of gas sensors with a special purpose heating system for utilizing the thermoelectric fluctuations.

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Biographies

Janusz M. Smulko was born in Kolno, Poland. He received his MSc and PhD degrees in electronics from Gdansk University of Technology, Poland, in 1989 and 1996, respectively. His doctoral research was in 1/*f* noise measurements in high-frequency bipolar transistors. Presently, he is working in Faculty of Electronics Telecommunication and Informatics, Gdansk University of Technology on problems of low frequency noise measurements and analysis. In 2003, he joined the Fluctuation and Noise Exploitation Laboratory at the Department of Electrical Engineering, Texas A&M University, Texas, USA as a NATO Post-Doctoral Fellow. His main research activity was concentrated on the application of 1/*f* noise measurements for gas sensing. He is a member of IEEE.

Jesper Ederth received his Master of Science degree in materials physics in 1998 at Uppsala University in Sweden. In January 2003 he obtained his PhD degree at the division of Solid State Physics at Uppsala University. His thesis dealt with electrical and optical properties of nanoparticle thin films of metals and highly doped semiconductors. During the spring of 2003 Dr. Ederth was a visiting scientist at the Fluctuation and Noise Exploitation Laboratory at the Department of Electrical Engineering, Texas A&M University, Texas, USA. From June until December 2003 he worked as a researcher at the Department of Materials Science at Uppsala University. In September 2003 he received the Benzelius award from the Royal Society of Science of Sweden for his research work summarized in his thesis.

Yingfeng Li received his PhD degree in electrical engineering from Texas A&M University, Texas, USA, in 1998. He is presently Visiting Research Scientist at the Department of Electrical Engineering, Texas A&M University. He worked for Applied Materials, Inc. and Advanced Micro Devices, Inc. from 1995 to 2003 as Electrical Engineer and Independent Contractor, respectively. He has published 19 papers in the area of fluctuation-enhanced sensing, semiconductor wafer fabrication, signal processing, and laser spectroscopy analysis. His current interests include wafer fabrication, fluctuation-enhanced sensing, and signal processing using neural network techniques. Dr. Li is a Senior Member of IEEE and Registered Professional Engineer of Texas.

Laszlo B. Kish (formerly Kiss) obtained the Doctoral Degree in solid state physics at the University of Szeged, Szeged, Hungary, in 1984. He is presently Associate Professor and Director of the Fluctuation and Noise Exploitation Laboratory at the Department of Electrical Engineering, Texas A&M University, Texas, USA. He is interested in a wide range of research topics related to noise, including condensed matters, complex systems, devices, nano systems, and bio systems. Dr. Kish is Editor-in-Chief of Fluctuation and Noise Letters. He is the founder of the conference series "Unsolved Problems of Noise" (1996 Szeged, Hungary; 1999 Adelaide, Australia; 2002 Washington, DC, USA). He is the founder and the Chair of the SPIE symposium series, "Fluctuations and Noise" (2003 Santa Fe, NM, USA; 2004 Canary Islands, Spain; 2005 Austin, Texas, USA). The Swedish Royal Society of Science has awarded him the year 2001 Benzelius Prize for his activities in the field of chemical sensing.

Marcus Kennedy studied material science at the Technical University Darmstadt in Germany. He obtained his PhD degree on the topic of the investigation of tin oxide (SnO_x) gas sensors based on monodisperse nanoparticle films at the University Duisburg-Essen. Since 2004 he has been working as a Project Engineer on alumina-silicon alloys for automotive and industrial application at PEAK Werkstoff GmbH, Velbert, Germany.

Frank Einar Kruis studied chemical engineering at the Technical University Delft in the Netherlands where he also obtained his PhD degree on the topic of aerosol reactors. He did research work on sintering behavior of aerosols at the University of Cincinnati (USA) as a visiting scientist. From 1993 to 1995 he did research work on turbulent particle interactions as post-doc at the ENSIC, Nancy, France. Afterwards he started his present research on nanoparticles as faculty member in the Engineering Department at University Duisburg-Essen in Germany and also obtained his Habilitation as 'Privatdozent'. He is recipient of the Von-Eucken Award of the Institute of German Chemical Engineers (GVC-VDI) and the Smoluchowski Award of the European Aerosol Society.