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Comparison of classical and fluctuation-enhanced gas sensing with Pd_xWO_3 nanoparticle films

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Abstract

Nanoparticle films of Pd_xWO_3, with x being 0.01 or 0.12, were made by dual-beam gas evaporation. The stochastic signal component (fluctuation-enhanced signal) originating from resistance fluctuations and the dc resistance (classical sensor signal) were measured during exposure to ethanol and hydrogen gas. For ethanol concentrations exceeding 50 ppm, changes in the resistance fluctuations gave 300 times larger detection sensitivity than changes in the dc resistance.

Keywords: Gas sensor; Gas detection; Gas evaporation; Resistance fluctuation; Tungsten oxide

1. Introduction

Gas sensing technology is a rapidly growing research field, for which improved sensitivity and selectivity are among the strongest driving forces. With regard to applications, other crucial aspects include durability and reproducibility [1,2]. A large number of investigations have been performed on gas sensors, particularly on those based on thin semi-conducting films for which changes in the dc transport have been used to probe a number of different target gases [3–13].

There are several types of sensors, utilizing different sensing mechanisms. The most common sensors comprise thin semiconducting metal oxide layers that can be reduced or oxidized by the gas, thereby changing their dc resistance [14] by modifying either the mobility or the concentration of the charge carriers. The mobility is likely to be altered by a gas-induced modification of the grain boundary potential between adjacent particles. A change in the charge carrier concentration can be due to surface-related electron traps. The magnitude of the resistance difference depends on the concentration of the target gas [1,2]. Thus the change in dc resistance - i.e., the sensitivity - is correlated to modifications of the dc transport parameters of the sensor caused by the target gas.

Gas sensors with improved sensitivity can be accomplished by fluctuation-enhanced sensing with measuring fluctuations in the resistance rather than changes in the dc resistance; the former are correlated to low frequency components of the dynamic disorder [15]. This fluctuation spectroscopy provides a new detection principle, as elaborated recently [14,16,17].

The purpose of this paper is to show that the gas detection ability of Pd_xWO_3 nanoparticle film sensors can be significantly improved by recording fluctuations in resistance. Our samples were porous films containing nanoparticles of WO_3 and Pd, prepared by gas evaporation [18–20]. Section 2 describes the sample preparation in detail. Considerations about some of the fundamental measures of fluctuation-enhanced sensing [14,16,17] are described in Section 3, and results related to gas sensing in air, ethanol, and hydrogen are presented

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in Section 4. Finally, the results are discussed and analyzed in Section 5.

2. Samples

2.1. Gas evaporation

All samples were made by gas evaporation. A schematic drawing of the gas evaporation unit is given in Fig. 1, showing that dual sources were used. A more detailed description of the equipment can be found elsewhere [18]. The left-hand source was employed for Pd evaporation. The starting material was put in a carbon crucible and was evaporated by induction heating. A laminar flow of synthetic air was used to cool the metal vapor so that nucleation and growth of Pd nanoparticles took place in the lower chamber. These nanoparticles were then transported to the upper chamber by the pressure difference between the two chambers. The right-hand evaporation source was used to form WO_3 nanoparticles by reactive evaporation. A tungsten pellet was heated by inductive heating. The surface of the pellet was then oxidized and sublimation led to the formation of WO_3 nanoparticles, which were brought to the upper chamber by the pressure gradient.

Films with a composition denoted Pd_xWO_3 were deposited onto Al_2O_3 substrates with pre-printed Au contacts on the top and a pre-printed Pt heating resistor on the back. The substrates were 8 mm × 8 mm in size, and the thickness of the evaporated Pd_xWO_3 film was approximately 1 μm. The concentration of Pd was controlled by varying the power of the induction heating. In practice, this power was set to a value in the 3.0–3.3 kW range, while the power used for heating the tungsten pellet was 1.0 kW. Two batches of samples were prepared; they are denoted A and B and are characterized by x being ∼0.01 and ∼0.12, respectively, the value of x was determined by Electron Spectroscopy for Chemical Analysis (ESCA) method [23]. All samples were post-deposition heat treated at 600 °C in air at atmospheric pressure for 1 h in order to produce structurally stable materials ready for gas detection measurements between room temperature and 350 °C.

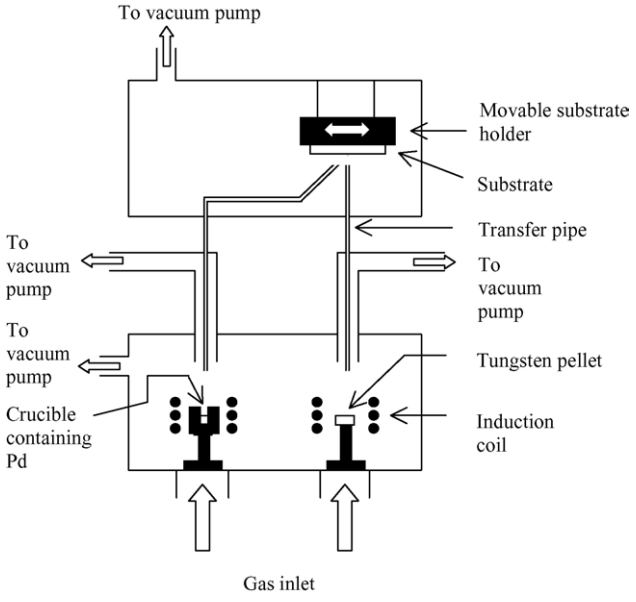

Fig. 1. Schematic drawing of the gas evaporation unit.

Note, in an earlier extensive study, Solis et al. [3] have prepared and characterized nanoparticle film samples of similar kinds at similar conditions. More information about the relevant structural properties can be found in [3].

3. Measurement and analysis techniques

3.1. Measurements

Pd_xWO_3 samples were placed in a stainless steel chamber with a volume of ∼1 dm^3 and were connected to a low-noise current generator. The resistance and the stochastic signal (voltage fluctuations) were then measured using a two-point method. The voltage fluctuations were amplified by a Stanford SR560 low-noise differential preamplifier and were sampled with a rate of 10 kHz by a PowerLab/4SP (AD Instruments) data acquisition unit. The power density spectrum (PDS) was calculated from the recorded stochastic signal [21]. Each recorded PDS exhibits a cut-off frequency corresponding to the RC time constant of the sample-cable-amplifier system. Gas concentrations were set by calibrated mass-flow controllers.

3.2. Sensitivity measures for gas detection

For comparison, we introduce several measures for the gas sensitivity of the samples. Thus $G_u(f)$ compares the spectra of voltage fluctuations measured in synthetic air and in the target gas:

$$G_u = \frac{S_u(f)_{sa}}{S_u(f)_{tg}} \quad (1)$$

where $S_u(f)$ is the PDS due to voltage fluctuations, and the subscripts sa and tg denote the synthetic air and the target gas, respectively. While $G_u(f)$ can be a useful measure when comparing sensors with similar current-drive conditions, its actual value depends on the driving current. Thus a more universal measure of sensitivity, $G_n(f)$, should be used for arbitrary driving currents. $G_n(f)$ compares the normalized voltage spectra, which are equal to the normalized resistance fluctuation spectra [14], in synthetic air and in the presence of a target gas:

$$G_n = \frac{\frac{S_n(f)_{sa}}{U_{sa}^2}}{\frac{S_n(f)_{tg}}{U_{tg}^2}} \quad (2)$$

where U is the measured dc voltage across the sensor. Finally, the dc resistance sensitivity G_{dc}, which is the classical measure, is defined as:

$$G_{dc} = \frac{R_{sa}}{R_{tg}} \quad (3)$$

where R is dc resistance of the sensor.

4. Data

4.1. General behavior of the spectra

Fig. 2 illustrates normalized spectra for two samples (one from each batch) measured at 350 °C for different target gases and applied dc voltages in the $0.2 < U < 1.2$ V range. The normalized spectrum $fS_u(f)/U^2$ was obtained by multiplying the voltage spectrum by the frequency and dividing it by the square of the dc voltage. The normalized spectra of different samples at different dc voltages look practically the same. Therefore the stochastic signals are caused by fluctuations in the resistance and not by other effects, such as thermal noise or fluctuations in the thermoelectric force due to a conceivably non-homogeneous temperature profile [22].

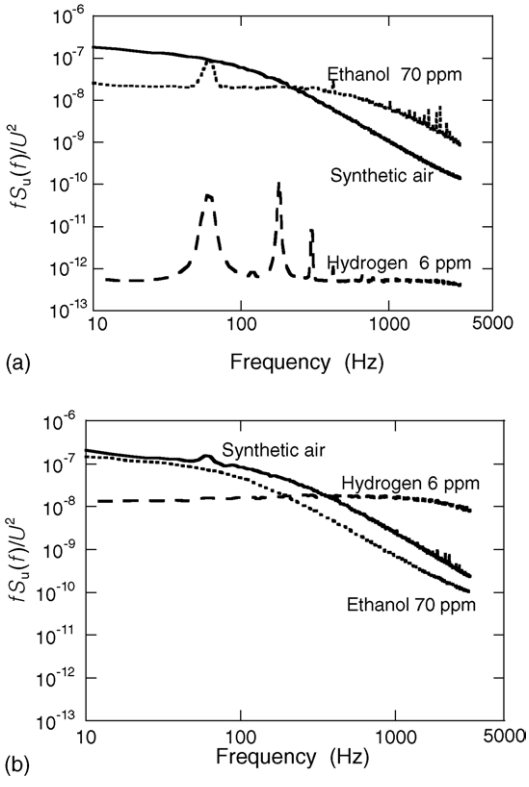

Fig. 2. Illustrative examples of normalized spectra recorded at 350 °C for Pd_xWO_3 samples. Parts (a) and (b) correspond to samples selected from batches A and B, respectively. The spikes on the spectra obtained with ethanol and hydrogen originate from the U.S. power line frequency (60 Hz and its harmonics).

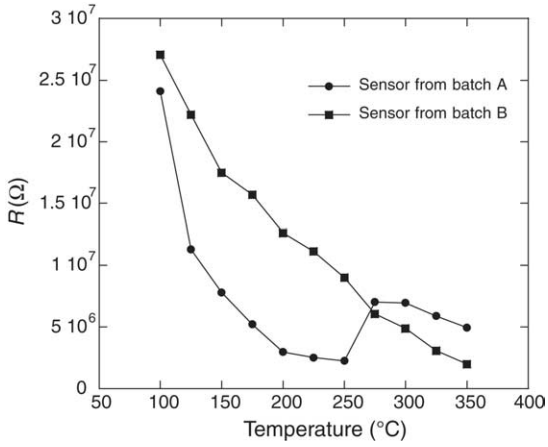

Fig. 3. Temperature-dependent resistance measured in synthetic air for Pd_xWO_3 samples originating from separate batches.

Another consequence of this observation is that the resistance fluctuations are independent of the electrical field or current in the sample.

From Fig. 2 it appears that samples from batch A show significantly different spectral patterns for synthetic air, ethanol, and hydrogen. Samples from batch B, on the other hand, yield slightly different patterns for synthetic air and ethanol and a significantly different behavior for hydrogen.

Fig. 3 presents the temperature dependence of the resistance for samples from the two batches as measured in synthetic air. It is observed that the sample from batch A shows a maximum at ∼275 °C. However, the sample from batch B does not exhibit a similar behavior, but the resistance decreases monotonically with increasing temperature.

4.2. Exposure to ethanol

The intensity of the voltage fluctuations became stabilized a few minutes after the introduction of the alcohol vapor. After the removal of the alcohol, the relaxation of the intensity of fluctuations took about five minutes, and the sensors exhibited very reproducible results.

Fig. 4 displays the response of the short-time-estimate of the noise voltage amplitude at 10 Hz for samples from batches A and B while exposed to 300 ppm of ethanol at 350 °C. Sample A shows fast response, high sensitivity with a variation of 3.5 orders of magnitude (3000 times), and good stability, while the corresponding properties of sample B are less favorable.

Fig. 5 presents the different measures of sensitivity for ethanol exposure to a sample from batch A. It is clearly observed that the sensitivity of the normalized resistance fluctuations G_n is up to 300 times higher than the dc resistance sensitivity G_{dc}, which is the sensor response classically used in Taguchi sensors.

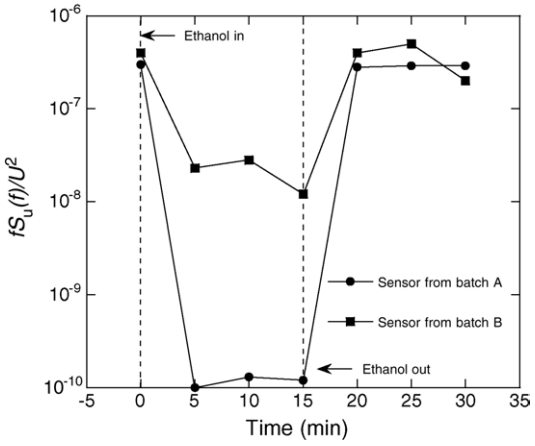

Fig. 4. Noise voltage amplitude at $f = 10$ Hz versus time upon application of 300 ppm of ethanol at 350 °C to Pd_xWO_3 samples from the two batches.

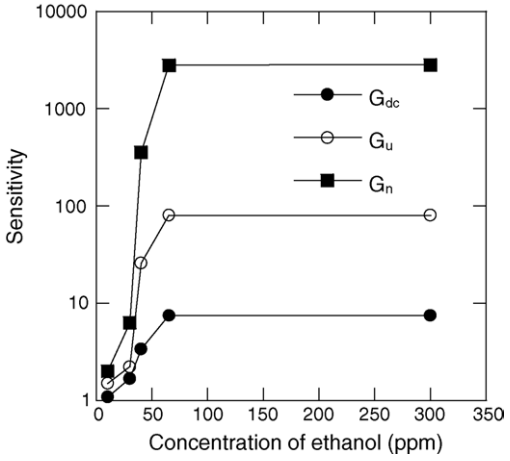

Fig. 5. Sensitivity, defined in three different ways as shown in Eqs. (1)–(3), at different concentrations of ethanol for a Pd_xWO_3 sample from batch A measured at 350 °C.

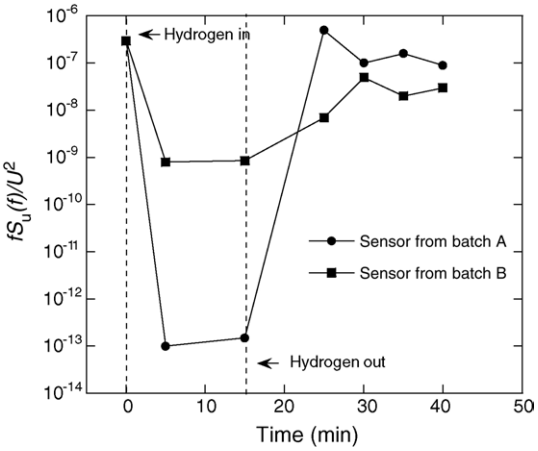

Fig. 6. Noise voltage amplitude at $f = 10$ Hz vs. time upon application of 1000 ppm of hydrogen at 350 °C to Pd_xWO_3 samples from the two batches.

4.3. Exposure to hydrogen

Fig. 6 shows noise voltage amplitude at 10 Hz versus time upon exposure to 1000 ppm of hydrogen gas. Initially the sensors gave very good response, with a variation of 6.5 orders of magnitude (3×10^6) for the sensor from batch A. However, after removing the hydrogen the fluctuation-enhanced signal showed memory effects and a strongly fluctuating value (not shown in Fig. 6). It is important to note that the application of a temperature pulse of 600 °C for 5 min did not remove this remaining effect of hydrogen. Thus hydrogen seems to act as a "poison" for this sensor.

5. Discussion

From the results presented in the previous sections, it is obvious that the resistance noise provides far better sensitivity than the dc resistance response. This may be a result of strong fluctuations in the grain boundary resistance due to the gas exposure being observable in the noise but not in the dc current. Further, relevant analysis of the possible origin of the stochastic component of the sensor signal was given elsewhere [14].

Samples from batch A contained only a very small amount of palladium. Because Pd nanoparticles can stimulate catalytic activity, our first expectation was that sensors from batch B would perform much better than sensors from batch A. However, the opposite effect was found and it is apparent that sensors from batch B provide poor noise sensitivity to ethanol, while sensors from batch A exhibit very good and reproducible results. The reason for this dichotomy is not known.

Further investigation is obviously needed not only to provide an explanation for the low sensitivity of sensors from batch B but also to study, in general, the effect of Pd on the fluctuation-enhanced sensitivity including the optimal amount of Pd doping in these nanoparticle films.

6. Conclusions

The main conclusion of this work is that using the fluctuation enhanced (stochastic) signal, instead of the dc resistance, can significantly improve the sensitivity of tungsten-oxide-based gas sensors. For example, at ethanol concentrations exceeding 50 ppm the fluctuation-enhanced sensitivity is at least 300 times larger than the dc resistance sensitivity.

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Biographies

Jesper Ederth received his Master of Science degree in materials physics in 1998 at Uppsala University in Sweden. In January 2003 he obtained his Ph.D. degree at the Division of Solid State Physics at Uppsala University. His thesis treated 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 thesis work.

Janusz M. Smulko was born in Kolno, Poland. He is a member of IEEE. He received the M.Sc. and Ph.D. degrees in electronics from Gdansk University of Technology, 80-952 Gdansk, ul. G. Narutowicza 11/12, 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, Tele-communication 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, College Station, TX, USA, as a NATO Post-Doctoral Fellow. His main research activity was concentrated on application of 1/*f* noise measurements for gas sensing.

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, College Station, TX, USA. He is interested in a wide range of research topics related to noise, including condensed matters, complex systems, devices, nanosystems, and biosystems. He is the founder and has been the 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 has been the Chair of the SPIE symposium series "Fluctuations and Noise" (2003, Santa Fe, NM, USA; 2004, Canary Islands, Spain; 2005, Austin, TX, USA). The Swedish Royal Society of Science has awarded him the Benzelius Prize for 2001 for his activities in the field of chemical sensing.

Claes-Göran Granqvist, born 1946, is Professor of Solid State Physics at the Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, Uppsala, Sweden, since 1993. He was formerly Professor of Experimental Physics at Chalmers University of Technology, Gothenburg, Sweden, in 1989–1993. Granqvist's research during the past several years has covered materials, especially thin films, for energy efficiency and solar energy applications particularly in the built environment. Variable-transmittance "smart" windows is one example. Other research interests include nanoscience and sensor science. Granqvist has published more than 500 scientific papers and many books and proceedings volumes. He is a member of the Royal Swedish Academy of Science and The Royal Swedish Academy in Engineering Sciences.