Fluctuation-Enhanced Multiple-Gas Sensing by Commercial Taguchi Sensors

Jose L. Solis, Gary E. Seeton, Yingfeng Li, *Senior Member, IEEE*, and Laszlo B. Kish

***Abstract*—This study is carried out to investigate and demonstrate the possibility of practical applications of commercial Taguchi gas sensors for fluctuation-enhanced chemical sensing of multiple gases. The stochastic resistance fluctuations of the sensors were studied during the burning-in process and during exposure to different gases at different temperatures. The analysis of resistance fluctuations in the gas sensors during and after exposure to gases indicates a strongly enhanced sensitivity and selectivity.**

***Index Terms*—Gas detectors, intelligent sensors, noise, spectral analysis.**

I. Introduction

SEMICONDUCTOR gas sensors are grainy film resistors with a large specific surface and a large surface current component. The chemical environment influences the surface conductivity and its fluctuations because the adsorbed chemical(s) and its fragments change the charge distribution and the electrical transport properties at the surface [1]. Recently, fluctuation-enhanced chemical sensing, a new method based on the measurement and analysis of the microscopic fluctuations in the signal of chemical sensors, was proposed to achieve enhanced sensitivity and selectivity [1]–[5]. The stochastic component of the sensor signal [6], [7], which has to be amplified before the analysis, carries a significant amount of information about the chemical environment. The statistical analysis of this signal can provide a pattern, for example, the power spectrum $S_u(f)$ of voltage fluctuations

$$S_u(f) = \frac{u_{\text{eff}}^2}{\Delta f} \tag{1}$$

where the u_{eff} is the effective (rms) voltage fluctuation in a narrow frequency band Δf around the frequency f. The spectrum $S_u(f)$ is characteristic of the ambient gas mixture. Investigations with Taguchi and surface acoustical wave sensors have shown that even a single sensor may be sufficient to realize an electronic nose [1]–[5].

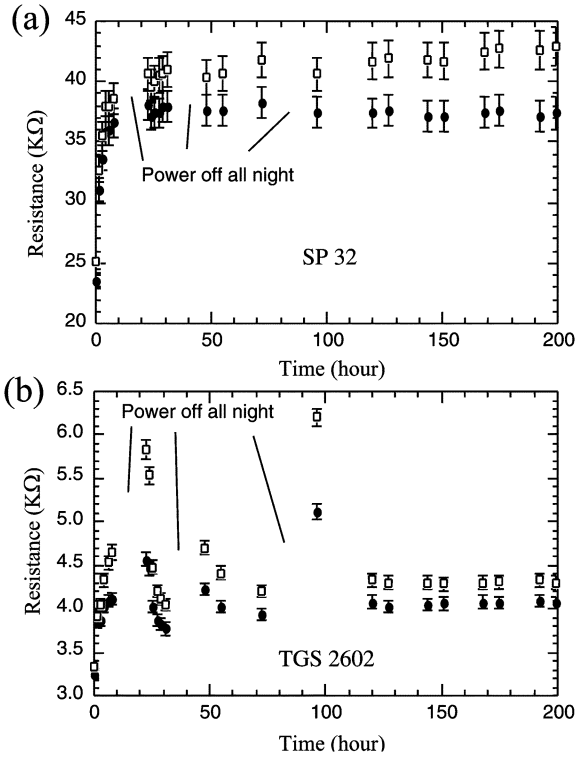

Fig. 1. Resistance versus time during the burning-in process in synthetic air of (a) SP 32 #1 (•) and SP32 #2 (□) and (b) TGS 2602 #1 (•) and TGS 2602 #2 (□) sensors. The applied heater voltage of these sensors during the burning-in process was 5 V. A dc current was not fed through the two terminals during the first three nights.

One of the most promising potential applications of fluctuation-enhanced chemical sensing is to develop a portable, versatile electronic nose with low power consumption and low maintenance due to the small number of sensors involved. However, the realization of such an electronic nose will need thorough studies about the nature of fluctuation-enhanced responses in commercial gas sensors at different operational temperatures and under different gas concentrations. A systematic methodology for selecting the best sensors for fluctuation-enhanced sensing would be of great importance.

In this paper, we study some practical aspects of the fluctuation-enhanced response in Taguchi-type sensors. The relevant fluctuations in Taguchi sensors are resistance fluctuations. Resistance (conductance) fluctuations occur in most conducting media and they usually show $1/f$ spectra in the low-frequency limit [8]–[12]. This is the situation even in conducting polymers where the noise is related to chemical information [11],

Manuscript received December 5, 2003; revised February 17, 2004. This work was supported by the Office of Naval Research and the Army Research Office. The associate editor coordinating the review of this paper and approving it for publication was Dr. Errol EerNisse.

J. L. Solis was with the Department of Electrical Engineering, Texas A&M University, College Station, TX 77843 USA. He is now with the Facultad de Ciencias, Universidad Nacional de Ingenieria, Lima, Peru (e-mail: jsolis@uni.edu.pe)

G. E. Seeton is with the Safety Engineering Office, Texas A&M University, College Station, TX 77843 USA (e-mail: garyseeton @aggienetwork.com).

Y. Li and L. B. Kish are with the Department of Electrical Engineering, Fluctuation and Noise Exploitation Laboratory, Texas A&M University, College Station, TX 77843 USA (e-mail: yingfeng@ee.tamu.edu; laszlo.kish@ee.tamu.edu).

Digital Object Identifier 10.1109/JSEN.2005.857882

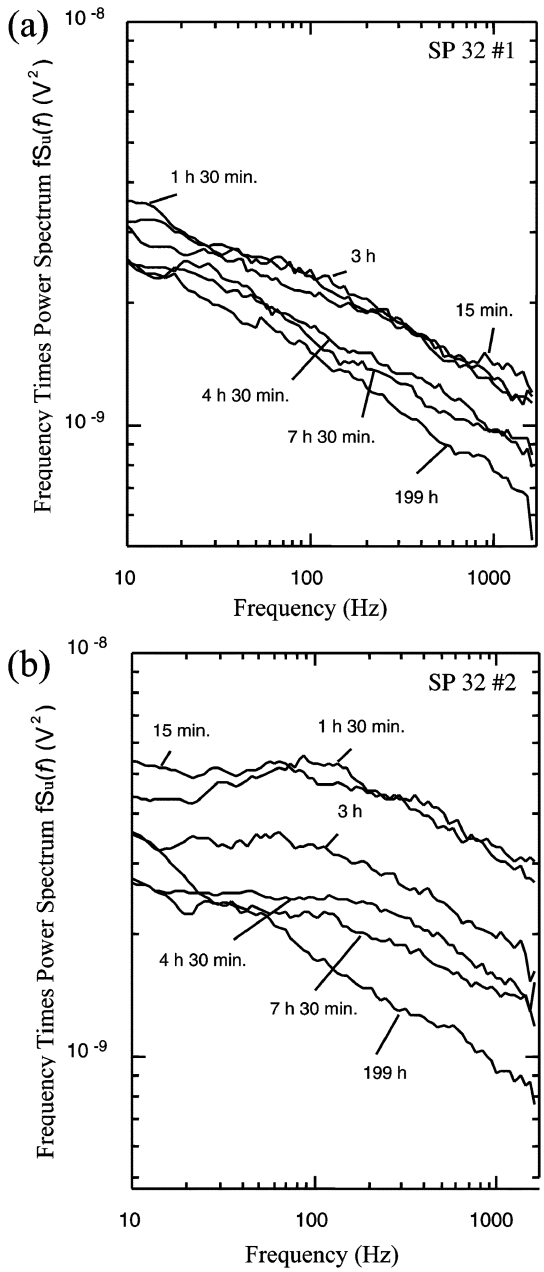

Fig. 2. Power spectra multiplied by frequency measured for (a) SP 32 #1 and (b) SP 32 #2 sensors at different time during the burning-in process in synthetic air. The burning-in time is indicated for each curve.

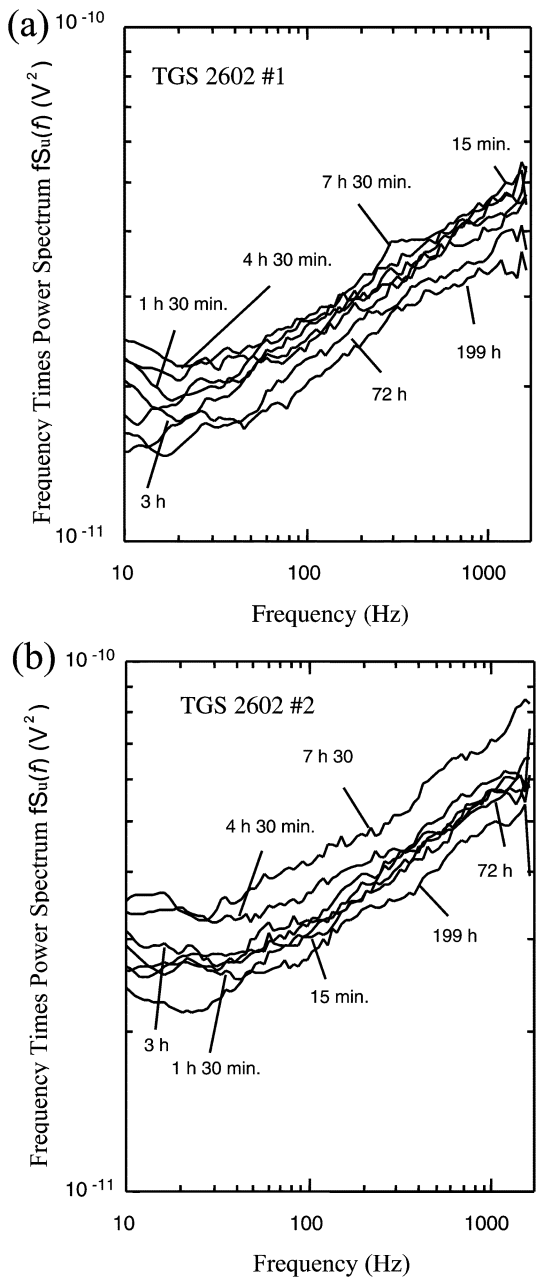

Fig. 3. Power spectra multiplied by frequency measured for the (a) TGS 2602 #1 and (b) TGS 2602 #2 sensors at different time during the burning-in process in synthetic air. The burning-in time is indicated for each curve.

[12]. This paper reports a systematic study for selecting commercial Taguchi type sensors for fluctuation-enhanced chemical sensing. The influence of temperature, aging, dc voltage, and ambient gas composition are also studied. We have tested the viability of normalized power spectra in the sensors, as tools for sensing.

II. Experiments

Commercial gas sensors manufactured by Figaro, Inc. (TGS 2602, TGS 2610, TGS 2611, and TGS 2620) and FIS, Inc. (SP 11, SP 19, SP 32, and SP 42A) were tested. These sensors are thick metal–oxide semiconductor films fabricated by a screen printing technique. The resistances of TGS 2602, TGS 2610, TGS 2611, and TGS 2620 sensors have a high sensitivity

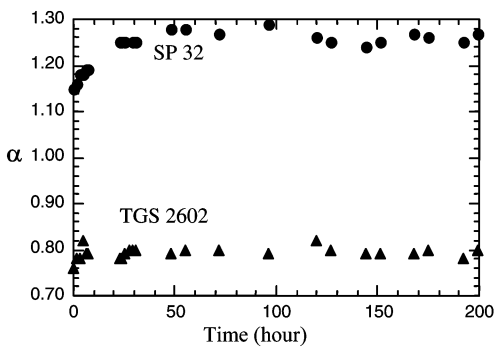

Fig. 4. The spectral exponent α versus burning-in time in synthetic air for SP 32 (•) and TGS 2602 (▲) sensors.

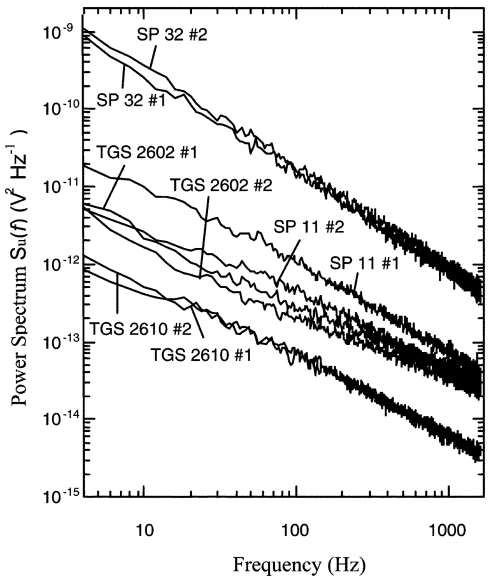

Fig. 5. Power spectra for SP 32, SP 11, TGS 2602, and TGS 2610 sensors in synthetic air after the burning-in process; #1 and #2 in the graph denotes two different sensors of each type of sensors.

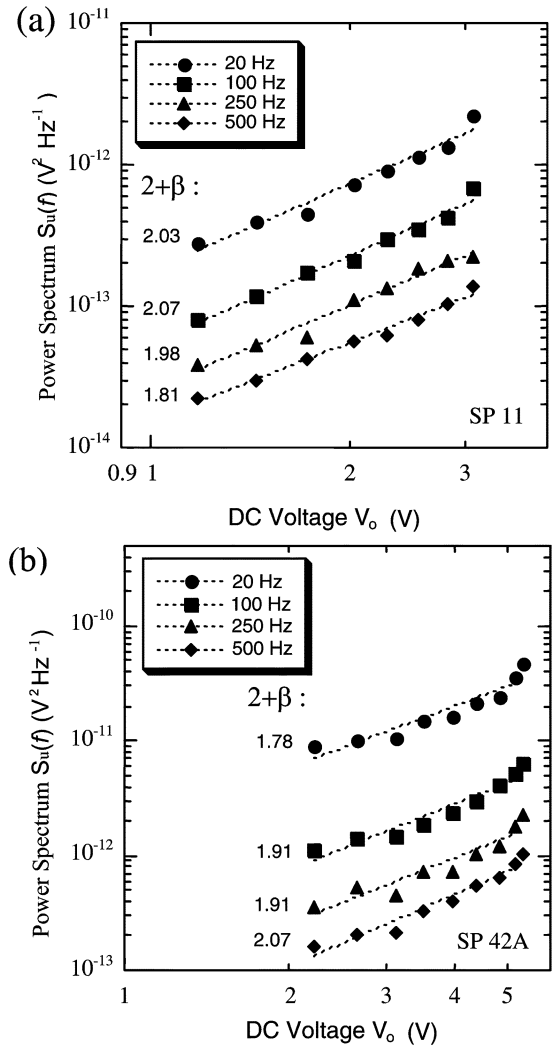

Fig. 6. Log–log plot for the power spectra at (•) 20 Hz, (■) 100 Hz, (▲) 250 Hz, and (♦) 500 Hz for (a) SP 11 and (b) SP 42A sensor as a function of the dc voltage V_o across the sample. The exponent value of V_o is indicated in the graph for the fitting of each set of data.

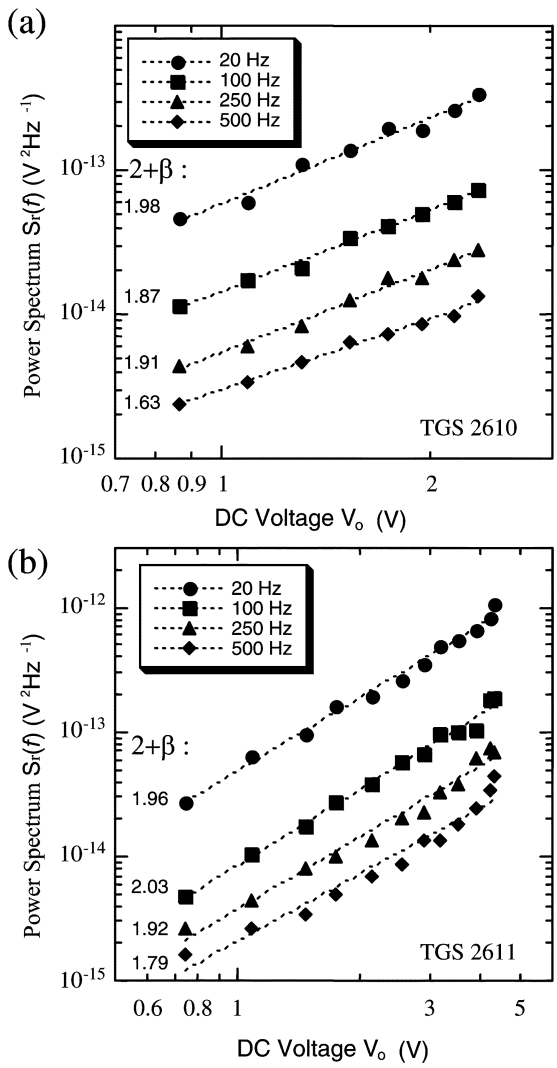

Fig. 7. Log–log plot for the power spectra at (•) 20 Hz, (■) 100 Hz, (▲) 250 Hz, and (♦) 500 Hz for (a) TGS 2610 and (b) TGS 2611 sensor as a function of the dc voltage V_o across the sample. The exponent value of V_o is indicated in the graph for the fitting of each set of data.

to alcohol and organic solvent vapors, to liquid petroleum gas and its components, to methane, and to volatile organic compounds and odor gases, respectively. The resistances of SP 11, SP 19, SP 32, and SP 42A sensors have a high sensitivity to hydrocarbons, hydrogen, alcohol, and refrigerant gas, respectively.

The samples under test were placed in a stainless steel Measurement Chamber of 700 cm^3 volume where multiple gases could be admitted via electronic gas flow controllers (Alicat Scientific, Inc.). The incoming gases were mixed by a diffusor after the controllers in order to have a homogeneous mixture and laminar flow. The Measurement Chamber can simultaneously accommodate four sensors. The gas sensing properties were investigated at various operating temperatures by applying different voltages to the integrated heaters of the sensors. We used synthetic air, nitrogen, and 300 ppm of ethanol in nitrogen as test gases.

The sensors contain four electrodes, two for measuring the film resistance and two for the heating of the substrate of the film. Thus, a standard two-probe resistance fluctuation test setup

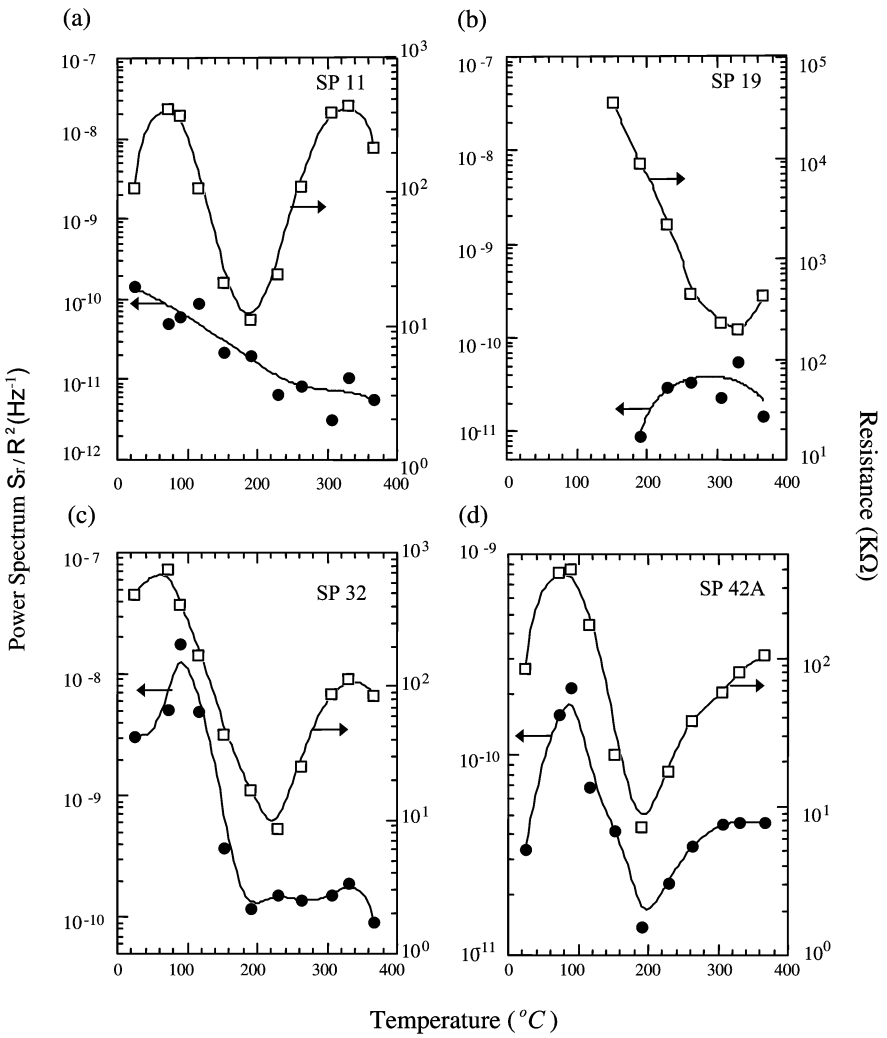

Fig. 8. Normalized spectra measured at (•) 20 Hz and the (□) sensor resistance versus temperature for (a) SP 11, (b) SP 19, (c) SP 32, and (d) SP 42A sensors in synthetic air. The solid lines are smooth curves through the data.

was used. The sensor films were driven by a low-noise dc current, which probed the resistance fluctuations, by the voltage fluctuations induced via Ohms law. The power spectrum of the voltage fluctuations $S_u(f)$ across the sensor was measured in the frequency range of 1 Hz–1.6 kHz by an SR 785 dynamic signal analyzer (Stanford).

III. Results and Discussions

A. Burning-in Process

The sensor manufacturers recommend a preheating of the sensors for typically two days before using the sensors. The applied heater voltage of these sensors recommended by the manufacturers was 5 V. The sensors under test were placed in a grounded stainless steel chamber for the burning-in process and 0.2 L/min of synthetic air was allowed to continuously flow through the chamber. The evolution of the resistances of SP 32 and TGS 2602 sensors during the burning-in period is shown in Fig. 1. Two of each type of sensor was tested. After the first day of heating, the sensor resistance reached a stable value. We observed that the resistance of the SP 32 [Fig. 1(a)] sensor was not affected when we fed a dc current through the two terminals of the heated sensor resistor during daytime and terminated the current feed (but not the heating) during nighttime. However, the resistance of TGS 2602 [Fig. 1(b)] was affected. Therefore, in order to have reproducible results, a stable dc current was fed through the two terminals of the sensor resistor during the entire experiment.

For a better indication of the difference between the shapes of the power spectra $S_u(f)$ of the voltage, the measured spectra were multiplied by the frequency f [1]–[5]. Fig. 2 shows $fS_u(f)$ of the voltage fluctuations measured for sensors SP 32 #1 and #2 at different times during the burning-in process. The initial spectra after 15 min of burning-in of both sensors were quite different. The spectrum of SP 32 #1 was very stable after 3 h of burning-in, but the spectrum of SP 32 #2 reached an equilibrium state after a total of 8 hours of burning-in. The spectra of both sensors were similar after the preheating process was completed. The other sensors showed similar behaviors.

The $fS_u(f)$ of the voltage fluctuations measured for sensors TGS 2602 #1 and #2 at different times during the burning-in process is shown in Fig. 3. The patterns of the spectra during the burning-in process were similar for both sensors. After 90 min of burning-in the spectra stabilized and had a small drift for the

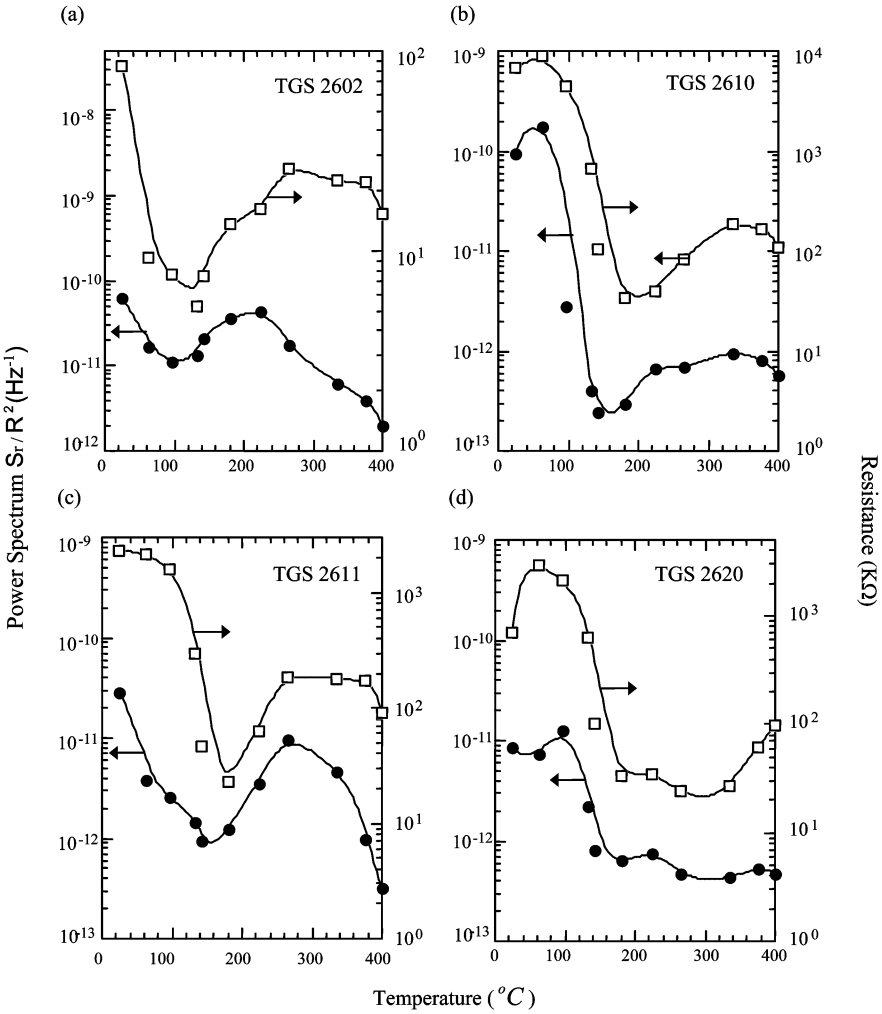

Fig. 9. Normalized spectra measured at (•) 20 Hz and the (□)resistance versus temperature for (a) TGS 2602, (b) TGS 2610, (c) TGS 2611, and (d) TGS 2620 sensors in synthetic air. The solid lines are smooth curves through the data.

rest of the burning-in time. The other sensors showed similar behaviors.

The spectra of the sensors over the measured range of frequency have approximately $1/f$ shape. A phenomenological equation describing the spectrum $S_u(f)$ of a resistor fed by a dc current generator can be given as

$$S_u(f) = \gamma V_o^{2+\beta} f^{-\alpha} \tag{2}$$

where V_o is the dc voltage across the sample, γ represents the strength of resistance fluctuations, β is the nonlinearity ($\beta = 0$ is the linear case), and α is the spectral exponent. Fig. 4 shows the variation of the mean of α with the burning-in time. The TGS 2602 sensor reached a stationary value almost immediately, whereas the SP 32 needed a day to achieve stabilization.

Fig. 5 displays typical spectra for TGS and SP sensors after the burning-in process in synthetic air. Each sensor type has a characteristic spectral pattern. The noise spectra for different TGS 2610, TGS 2602, and SP 32 sensors of the same type are very similar. However, the spectra of different SP 11 sensors have somewhat different patterns. Therefore, the phenomenon that produced the resistance fluctuations has a good reproducibility, which indicates a well-controlled film technology [6], [7].

B. Voltage Dependence of the Noise

The I–V characteristics of the sensors were linear with no significant deviation from Ohmic behavior over the full range of applied voltages. Figs. 6 and 7 show the log–log plots of the spectra at four different frequencies for the TGS and SP sensors as a function of the dc voltage V_o. The straight lines represent fits based on the proportionality relation between $S_u(f)$ and $V_0^{2+\beta}$ as seen in (1). The value of β is approximately zero for the TGS and SP sensors. This behavior indicates that the current does not influence the resistance fluctuations. Instead it only probes the resistance fluctuations via Ohm's law. This fact allows us to infer that we observe equilibrium resistance fluctuations [7].

C. Temperature Dependence of the Noise

The voltage applied to the integrated heater controls the temperature of the gas-sensing film in the sensor. The temperature, as evaluated from the resistance of the heater element, was varied in the range of 25–400 °C. The resistance of the sensors changed with temperature, so we evaluated the normalized spec-

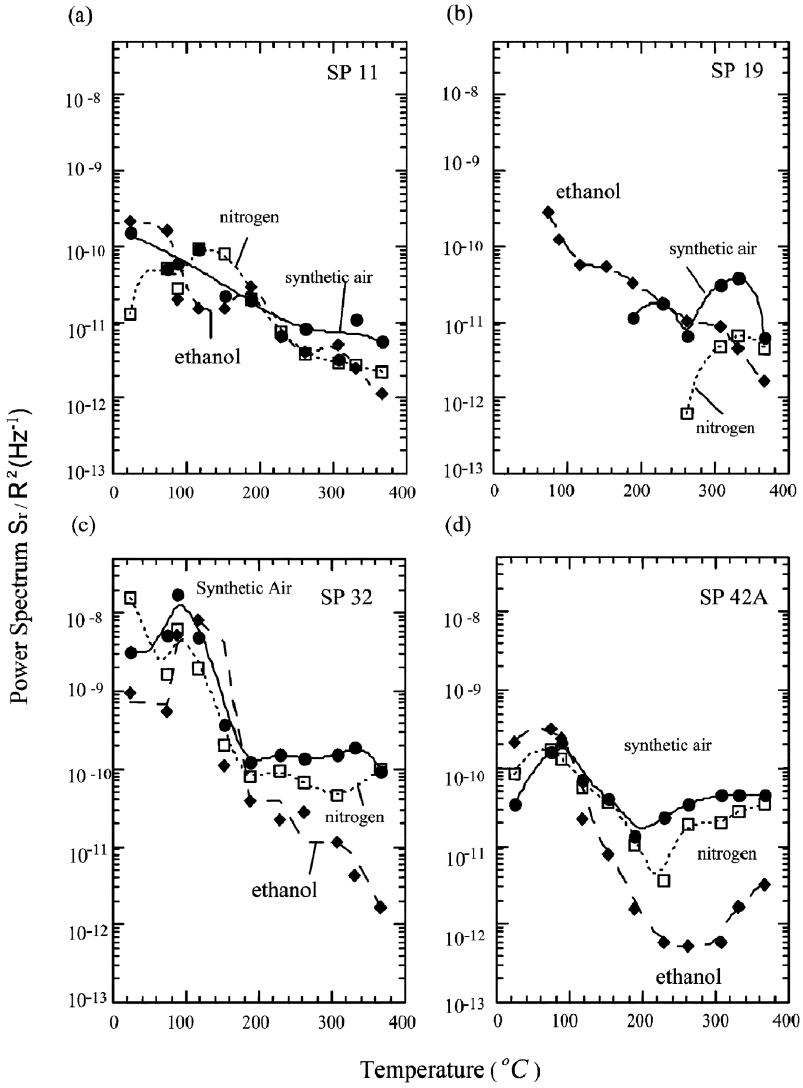

Fig. 10. Normalized spectra measured at 20 Hz versus temperature for (a) SP 11, (b) SP 19, (c) SP 32, and (d) SP 42A sensors in (•) synthetic air, (□) nitrogen, and (◊) 300 ppm of ethanol in nitrogen. The lines are the smooth curves through the data.

trum $S_r(f)/R^2$, where $S_r(f)$ and R are the resistance spectrum and the resistance, respectively. Figs. 8 and 9 show the temperature dependence of the resistance and the normalized spectra measured at 20 Hz in the SP and TGS sensors. The temperature dependence of the normalized noise and that of the resistance are very similar in sensors TGS, SP 32 and 42A. However, the variations of the normalized spectrum and the resistance in SP 19 and SP 11 sensors are very different.

We note that the range of 10–30 Hz is important for practical applications. The reason is twofold. Firstly, these kinds of fluctuations have a 1/f like power density spectra so the lower the frequency, the higher the noise. However, a frequency which is too low would require excessive recording and averaging times. Second, in the case of weak fluctuations and/or strong electromagnetic interference, the 60 Hz and its higher harmonics can negatively influence the accuracy and reproducibility of the measurements. However, this situation can be avoided by maintaining a frequency below 60 Hz.

The temperature dependent analysis of the spectral exponent, based on the Dutta and Horn [8] model, indicates that the resistance fluctuations are not a thermally activated random process; instead, the potential barriers of microscopic fluctuator elements depend on the temperature, see below. The sensing layer in a semiconductor gas sensor is a porous material, and the electric current flows through the grain boundary junctions. According to simple models [13], [14], at the grain boundaries, the adsorbed oxygen forms an energy barrier. This energy barrier controls the resistance of the junction. The energy barrier has a strong dependence on the temperature and gas concentration [13]. Ambrozy [14] found that a barrier-dominated contact model would show the following temperature dependence

$$S_r(T)R^{-2}(T) \propto R^x(T) \tag{3}$$

where $x = 2$. With our results, we found $x < 1$; so, this model canot explain the temperature dependence. The most likely reason for this particular behavior is that the energy barriers themselves have strong temperature dependence, as indicated by Lantto and coworkers [13].

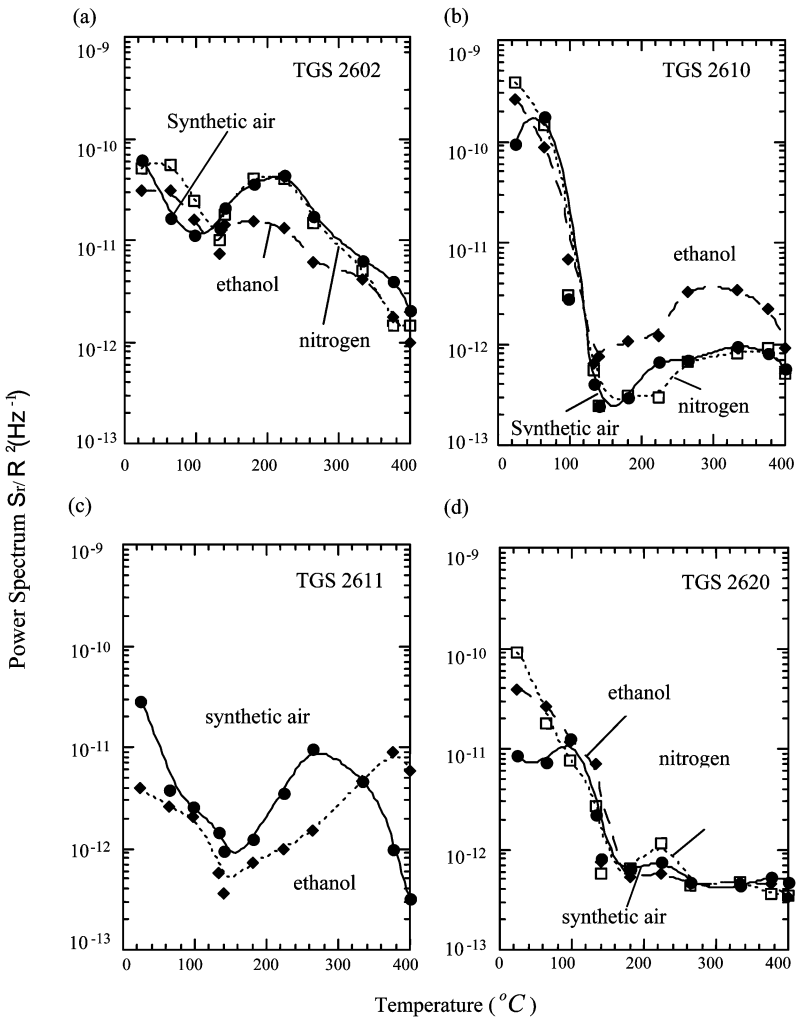

Fig. 11. Normalized spectra measured at 20 Hz versus temperature for (a) TGS 2602, (b) TGS 2610, (c) TGS 2611, and (d) TGS 2620 sensors in (•) synthetic air, (□) nitrogen, and (◊) 300 ppm of ethanol in nitrogen. The lines are the smooth curves through the data.

D. Influence of the Ambient Gas Mixture

To study the effect of the ambient gas composition on the sensor response, sensors were placed in the measurement chamber and 0.2 L/min gas was allowed to continuously flow through the chamber. These gases were synthetic air, nitrogen or 300 ppm of ethanol in nitrogen. Figs. 10 and 11 show the temperature dependence of the normalized spectra at 20 Hz of the SP and TGS sensors in synthetic air. The synthetic air and nitrogen produced a similar pattern for the TGS and SP sensors; therefore, it is impossible to distinguish between these two atmospheres with these sensors. The patterns produced by the SP 32 [Fig. 10(c)], SP 42A [Fig. 10(d)], TGS 2610 [Fig. 11(b)], and TGS 2611 [Fig. 11(c)] sensors with 300 ppm of ethanol in nitrogen are very different from the patterns in synthetic air and nitrogen. The pattern for SP 11 [Fig. 10(a)] in ethanol demonstrates a small difference for the nitrogen and synthetic air atmospheres. However, the patterns for SP 19 [Fig. 10(b)], TGS 2602 [Fig. 11(a)], and TGS 2620 [Fig. 11(d)] in nitrogen, ethanol, and synthetic air are similar.

The resistance of the TGS 2602 sensor has a high sensitivity to alcohol, but its normalized noise spectra in ethanol and synthetic air are similar. The SP 32 sensor is also sensitive to alcohol and the corresponding noise spectra have different patterns. The normalized noise spectra for SP 42A in ethanol and synthetic air are very different, even though this sensor is classically used for refrigerant gases. The noise in the SP sensors due to ethanol vapor is higher than the noise in synthetic air. On the other hand, the noise detected in TGS sensors due to ethanol is lower than the noise detected in synthetic air. This is additional information to the resistance change. These results indicate the following.

1) A single sensor developed for a certain gas can be used to identify other gases, too. Note that certain gases are exceptions.
2) A single sensor has the potential to be used as a complex electronic nose for the detection of various gas compositions.
3) The spectral responses of the different gases are not additive. Thus, the need to train a neural network to recognize the spectra at various gas compositions seems to be unavoidable in practical applications.

IV. Conclusion

We have applied a systematic study to explore the applicability of using commercial Taguchi sensors for fluctuation-en-

hanced electronic nose applications. The sensors need a preheating for one day in synthetic air in order to have reproducible data. The power spectra of the sensors are characteristic for each sensor and are $1/f$ like. The dependence of the spectra on the dc voltage in these sensors indicates that equilibrium resistance fluctuations are present.

ACKNOWLEDGMENT

The authors would like to thank G. Schmera for valuable discussions.

REFERENCES

[1] L. B. Kish, R. Vajtai, and C. G. Granqvist, "Extracting information from noise spectra of chemical sensors: Single sensor electronic noses and tongues," *Sens. Actuators*, vol. 71, pp. 55–59, 2000.

[2] J. L. Solis, G. Seeton, Y. Li, and L. B. Kish, "Fluctuation-enhanced sensing with commercial gas sensor," *Sens. Transducers*, vol. 38, pp. 59–66, 2003.

[3] J. L. Solis, L. B. Kish, R. Vajtai, C.-G. Granqvist, J. Olsson, J. Schnurer, and V. Lantto, "Identifying natural and artificial odours through noise analysis with a sampling-and-hold electronic nose," *Sens. Actuators B*, vol. 77, pp. 312–315, 2001.

[4] J. Smulko, C.-G. Granqvist, and L. B. Kish, "On the statistical analysis of noise in chemical sensors and its application for sensing," *Fluct. Noise Lett.*, vol. 1, pp. L147–L153, 2001.

[5] G. Schmera and L. B. Kish, "Fluctuation-enhanced gas sensing by surface acoustic wave devices," *Fluct. Noise Lett.*, vol. 2, pp. L117–L123, 2002.

[6] Y.-K. Yong and J. R. Vig, "Modeling resonator frequency fluctuations induced by adsorbing and desorbing surface molecules," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 37, no. 3, pp. 543–550, Jun. 1990.

[7] J. R. Vig and Y. Kim, "Noise in microelectromechanical system resonators," *IEEE Trans. Ultrason., Ferroelectr., Freq. Contr*, vol. 46, no. 5, pp. 1558–1565, Oct. 1999.

[8] P. Dutta and P. M. Horn, "Low-Frequency fluctuation in solids: $1/f$ noise," *Rev. Mod. Phys.*, vol. 53, pp. 497–516, 1981.

[9] M. B. Weissman, "$1/f$ noise and other slow, non exponential kinetics in condensed matter," *Rev. Mod. Phys.*, vol. 60, pp. 537–571, 1988.

[10] L. B. Kiss, "On fluctuations with a $1/f$ spectrum and the nonexistence of the quantum $1/f$ noise effect," *Rev. Solid State Sci.*, vol. 2, pp. 659–678, 1988.

[11] P. Bruschi, F. Cacialli, A. Nannini, and B. Neri, "Gas vapor effects on the resistance fluctuation spectra of conducting polymer thin-film resistors," *Sens. Actuators*, vol. 18–19, pp. 421–425, 1994.

[12] P. Bruschi, A. Nannini, and B. Neri, "Vapor and gas sensing by noise measurements on polymeric balanced bridge microstructures," *Sens. Actuators B*, vol. 24–25, pp. 429–432, 1995.

[13] V. Lantto, P. Romppainen, and S. Leppävouri, "A study of the temperature dependence of the barrier energy in porous tin dioxide," *Sens. Actuators B*, vol. 14, pp. 149–163, 1988.

[14] A. Ambrozy, "$1/f$ noise in (BaSr) TiO_3 (barrier-dominated contact noise)," *IEEE Trans. Electron Devices*, vol. ED-28, no. 3, pp. 344–346, Mar. 1981.

Jose L. Solis was born in Concepcion, Peru, in 1965. He received the Ph.D. degree in physics from the Universidad Nacional de Ingenieria, Lima, Peru, in 1997.

He has carried out research in Brazil, Finland, Sweden, and the USA. From 1997 to 1998, 1999 to 2000, and 2002, he was a Postdoctoral Researcher with the University of Oulu, Oulu, Finland; Uppsala University, Uppsala, Sweden; and Texas A&M University, College Station, respectively. He is currently an Associate Professor at the Science Faculty, Universidad Nacional de Ingenieria, and Researcher with the Peruvian Nuclear Institute (IPEN). His research interests are currently focused on materials for gas sensors, electrochromism, and photocatalysis. He has published more than 20 papers.

Gary E. Seeton was born in Denver, CO, in April 1949. He received the Ph.D. degree in interdisciplinary engineering from Texas A&M University, College Station, in 2003.

He is currently with the Safety Engineering Office of Texas A&M Univeristy. He has worked in industry as a Health Physicist and as the Director of Technology for both a laser manufacturer and an instrument R&D firm. He has done research for and developed instrumentation for various labs in material science, electrical engineering, and safety engineering.

Yingfeng Li (SM'03) received the Ph.D. degree in electrical engineering from Texas A&M University, College Station, in 1998.

He is currently a Visiting Research Scientist at the Department of Electrical Engineering, Texas A&M University. He was with 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 fluctuation-enhanced sensing, wafer fabrication, and signal processing using neural network techniques.

Dr. Li is a Registered Professional Engineer of Texas.

Laszlo B. Kish (formerly Kiss) received the doctoral degree in solid state physics at the University of Szeged, Szeged, Hungary, in 1984.

He is currently an Associate Professor and Director of the Fluctuation and Noise Exploitation Laboratory, Department of Electrical Engineering, Texas A&M University, College Station. He is interested in a wide range of research topics related to noise, including condensed matters, complex systems, devices, nanosystems, and biosystems.

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). He is the Founder and the Chair of the SPIE symposium series "Fluctuations and Noise" (2003, Santa Fe, NM; 2004, Canary Islands, Spain; 2005, Austin, Texas). The Swedish Royal Society of Science awarded him the 2001 Benzelius Prize for his activities in the field of chemical sensing.