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Fluctuation-Enhanced Sensing with Commercial Gas Sensors

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Abstract: The stochastic component of the sensor signal in commercial semiconductor gas sensors during exposure to different gases has been studied. The resistance fluctuation measurements have been carried out using different concentrations of ethanol, CO, NO_x, H_2 and SO_2 in dry synthetic air. The analysis of the stochastic resistance fluctuations in gas sensors during exposure to gases enables an enhanced sensitivity and selectivity. The normalized power spectrum is characteristic for each sensor, and each gas induces a new characteristic power spectrum. In many cases, sensors can be used even for different gases than the gas they were originally designed for.

Keywords: electronic nose, gas sensing, electronic tongue, stochastic sensing, 1/f noise.

1. Introduction

Semiconductor gas sensors based on SnO_2 are widely used as safety monitors for detecting most combustible and pollution gases. However, most of the commercial gas sensors are not selective enough to detect a single chemical species in a gaseous mixture. It is desirable that a single sensor should be able to selectively detect several kinds of gases. Previously, multiple gas identification efforts with a single sensor had assumed a particular temperature modulation, either sinusoidal with a fixed frequency [1, 2] or cyclic heating such as linear ramps [3]. However, trials to implement a practical usage of such systems seem to have been lacking. The main problem to be overcome is still the non-linearity of the sensor response.

Recently, in different efforts, it has been shown that microscopic fluctuation of the resistance of the chemical sensor contains more information about the measured chemical than the mean value of the

resistance. The effect of various vapors on the power spectra of the resistance fluctuations has been studied for conducting polymer thin-film resistors [4, 5]. The interaction of the chemical with the surface and bulk of the sensor induces spontaneous fluctuations. Recently, new methods [6, 7] have been proposed for chemical sensing that utilizes the analysis of the stochastic component of the sensor signal in Taguchi type sensors. It has been shown that even a single sensor may be sufficient for realizing a powerful electronic nose. However, there are no studies of the power spectrum in different types of commercial gas sensors under different gas atmospheres. This paper studies the stochastic signal in commercial semiconductor gas sensors measured under different atmospheres. Ethanol, H_2, CO, NO_x and SO_2 at various concentrations in dry synthetic air (20 % O_2 and 80 % N_2) were used as test gases.

2. Experiment

The commercial gas sensors manufactured by Figaro Inc. (TGS sensors) and FIS Inc. (SP sensors) were used. The sensing material in these sensors is comprised of a SnO_2 on an aluminum substrate together with an integrated heater. Four different types of gas sensors from each company were used. The TGS 2602, TGS 2610, TGS 2611 and TGS 2620 sensors have a high sensitivity to alcohol and organic solvent vapors, liquid petroleum gas and its component gases, methane, volatile organic compounds (VOCs) and odor gases, respectively. The SP 11, SP 19, SP 32 and SP 42A sensors have a high sensitivity to hydrocarbons, hydrogen, alcohol and refrigerant gas, respectively.

Up to four sensors can be placed into the grounded stainless steel chamber where gas compositions can be admitted with gas flow controllers manufactured by Alicat Scientific, Inc.. The measurement cell has a volume of 700 cm^3 and the gas flow was kept at 500 ml/min. The measurements have been carried out using different concentrations of ethanol, CO, NO_x, H_2 and SO_2 in dry synthetic air.

A stable DC current was fed through the two terminals of the sensor film by a low-noise current generator (battery-based). The driving DC current induces voltage fluctuations due to resistance fluctuations in the sensor, due to Ohm's law. The power spectrum of amplified voltage fluctuations across the sensor was measured utilizing a Stanford Research Systems model SR 785 dynamic signal analyzer. The power spectrum $S_u(f)$ of the stochastic voltage fluctuations was measured in the frequency range of 1 Hz - 1.6 kHz. The measurements were done after the stabilization of the sensor resistance, usually 20 minutes after the atmosphere was introduced. The resistance R of the sensor also changes with the atmosphere, so we have evaluated the normalized resistance fluctuation spectrum $S_r(f)/R^2$, where $S_r(f)$ is the spectrum of resistance fluctuations.

3. Results and Discussion

The sensor manufacturers recommend preheating (burning-in) of the sensor for 2 days before using it. We have observed that the power spectra of the sensors stabilize after about one day. In synthetic air, the power spectra of the sensors over the measured range of frequencies scales approximately as $1/f$. The sensors have no significant deviation from the ohmic behavior over the full range of applied voltages. The strength of the measured voltage fluctuations is proportional to the square of the applied DC voltage, so resistance fluctuations explain the spectra [8,9].

In order to enhance the visible difference between the shapes of the spectra, the measured spectra were multiplied by frequency. Fig. 1 shows the normalized spectra multiplied by the frequency measured in dry synthetic air for the SP and TGS sensors. The spectrum of the sensors in synthetic air is characteristic for each sensor. The normalized spectra measured during exposure to 60 ppm ethanol in

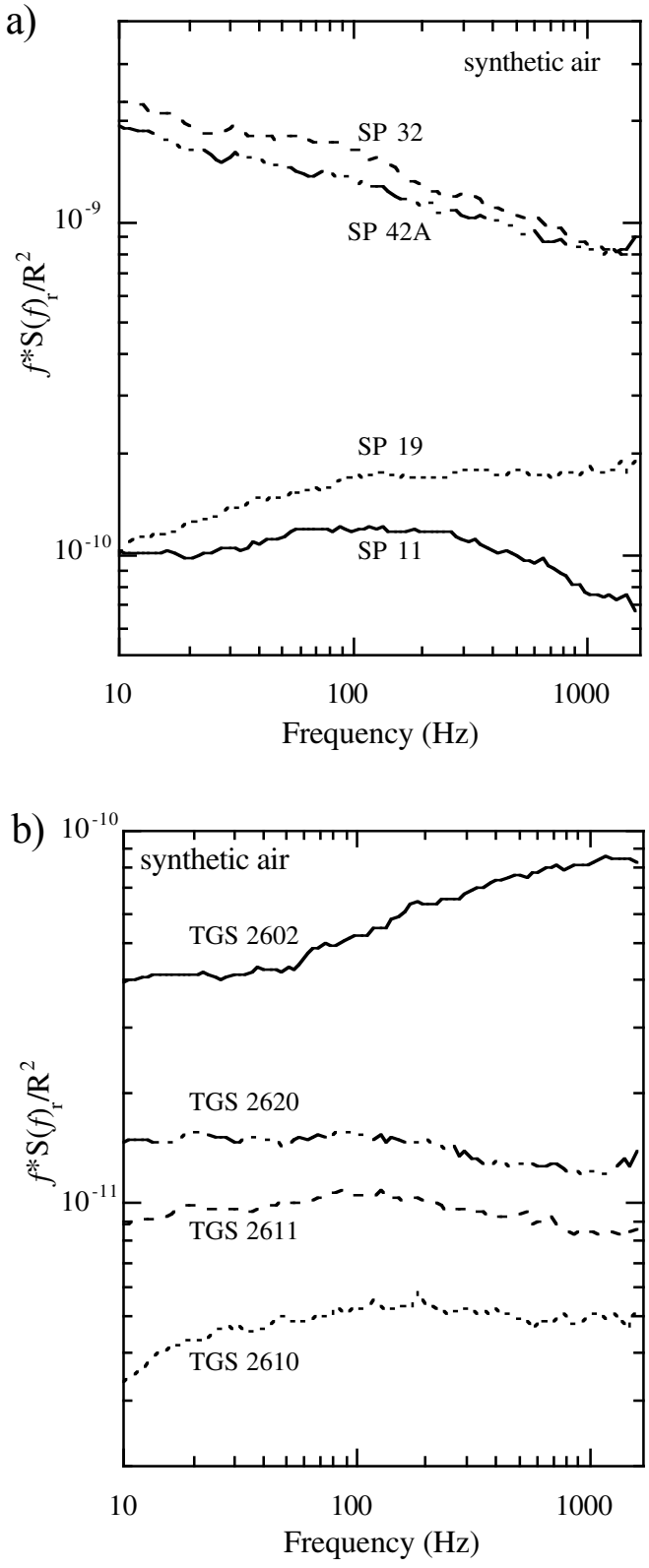

Fig. 1. *Normalized (power) spectra multiplied by the frequency measured in synthetic air for (a) the SP 11 (solid line), SP 19 (doted line), SP32 (dashed line) and SP 42A (dashed and doted line) sensors, and (b) TGS 2602 (solid line), TGS 2610 (dashed line), TGS 2611 (dashed line) and TGS 2620 (dashed and doted line) sensors.*

synthetic air and 233 ppm hydrogen in synthetic air for SP and TGS sensors are shown in Fig. 2 and Fig. 3, respectively. The SP sensors have different spectra for ethanol and synthetic air (Fig. 2). The SP 11 and SP 42A sensors also have clearly different spectra for hydrogen. However, the SP 19 and SP 32 sensors have similar spectra for hydrogen and synthetic air. The TGS 2610 and TGS 2611 sensors have different spectra for each atmosphere (Fig. 3). The TGS 2602 sensor can clearly differentiate between synthetic and ethanol. However, the spectra from hydrogen and synthetic air are similar. The TGS 2620 sensor could not differentiate the different atmospheres.

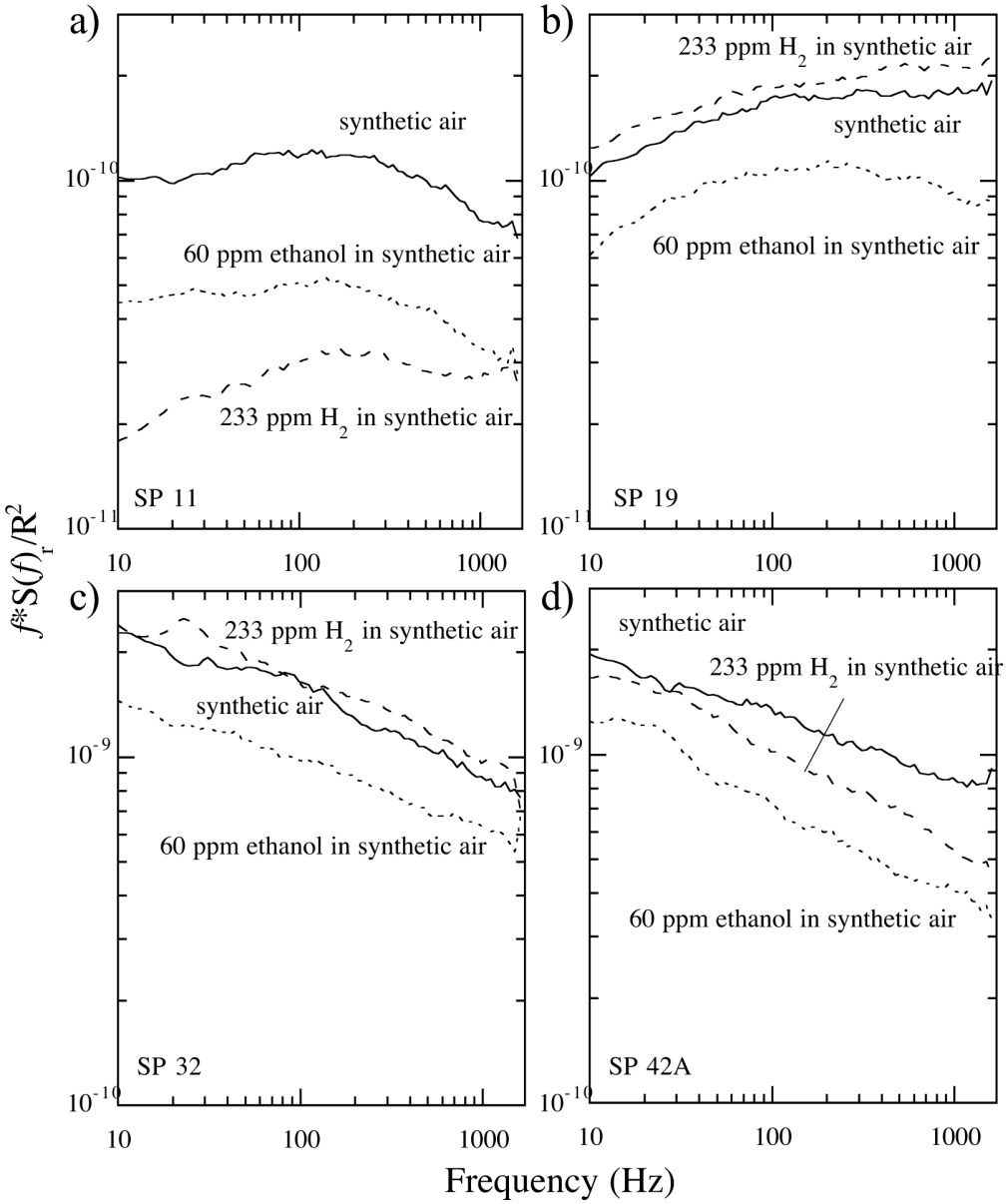

Fig. 2. *Normalized spectra multiplied by the frequency measured in synthetic air (solid lines), 60 ppm ethanol in synthetic air (doted lines) and 233 ppm H_2 in synthetic air (dashed lines) for (a) SP 11, (b) SP 19, (c) SP 32 and (d) SP 42A sensors.*

To evaluate the changing of spectra with the gas concentration, they were measured with different ethanol concentrations in synthetic air. Fig. 4 shows the normalized power spectra multiplied by the frequency for different concentrations of ethanol in synthetic air for TGS 2610 and SP 32 sensors. The

TGS 2610 sensor could detect low concentrations of ethanol in synthetic air, and has a saturation effect for higher concentrations than 100 ppm (Fig. 4a). The SP 32 sensor could detect low concentrations of ethanol in synthetic air like 7.3 ppm (Fig. 4b), and has no saturation effect for concentrations up to 150 ppm. The spectrum for synthetic air remains the same after exposure to different concentrations of ethanol. A change in the concentration of the gas produces different spectra that can be used to quantify the concentration of the gas in the atmosphere.

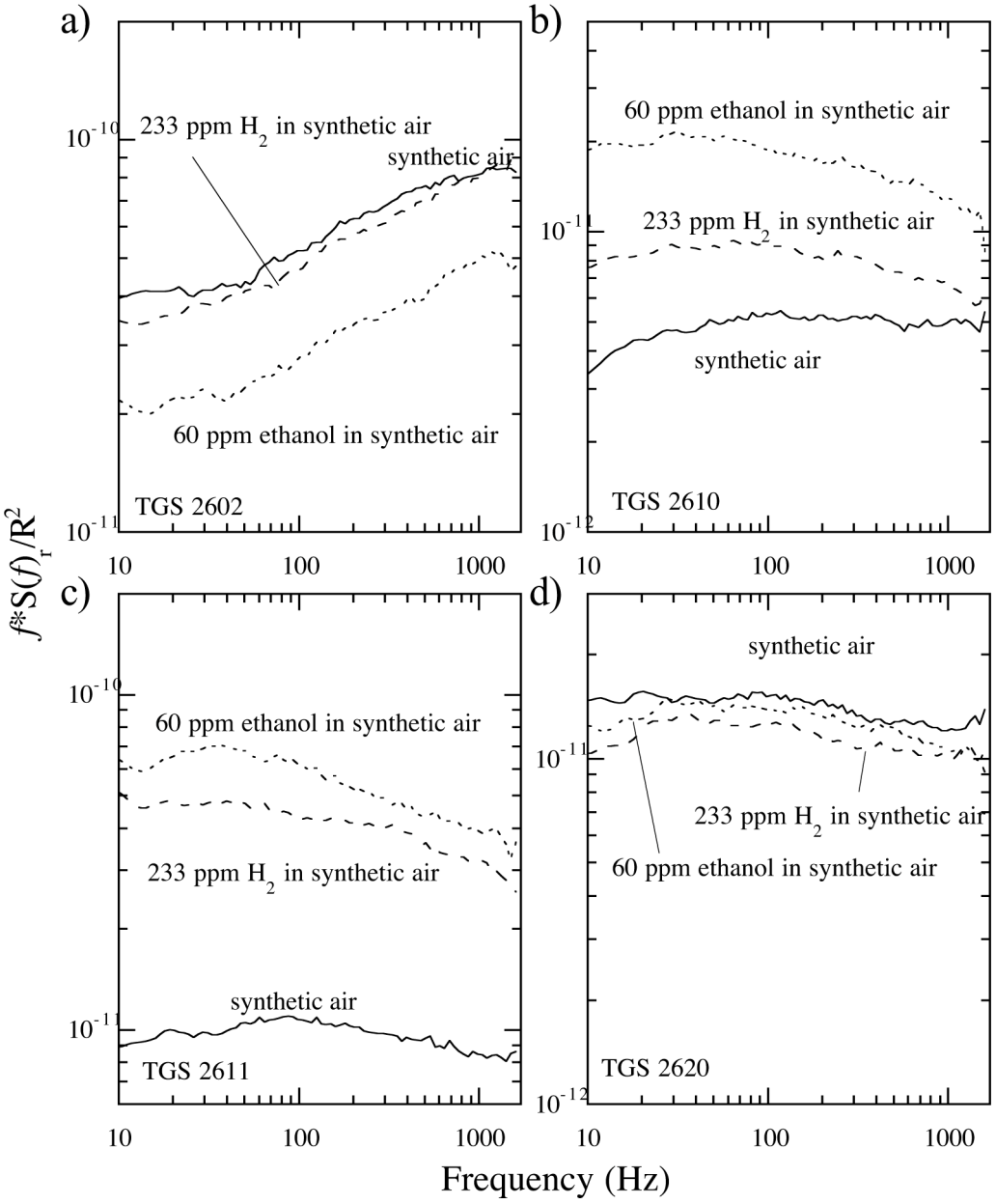

Fig. 3. *Normalized (power) spectra multiplied by the frequency measured in synthetic air (solid lines), 60 ppm ethanol in synthetic air (doted lines) and 233 ppm H_2 in synthetic air (dashed lines) for (a) TGS 2602, (b) TGS 2610, (c) TGS 2611 and (d) TGS 2620 sensors.*

The identification of gases in a mixture is of practical importance, so we measured the sensors during exposure to different binary mixtures. The various spectra observed for pure gases and their mixture are shown in Fig. 5 for the TGS 2610 sensor. The mixture of ethanol and NO_x has a slightly different spectrum than the one with ethanol (Fig. 5 a). However, spectra at binary mixtures of SO_2 and ethanol

have noticeably different spectra than that of any single gases tested (Fig. 5b).

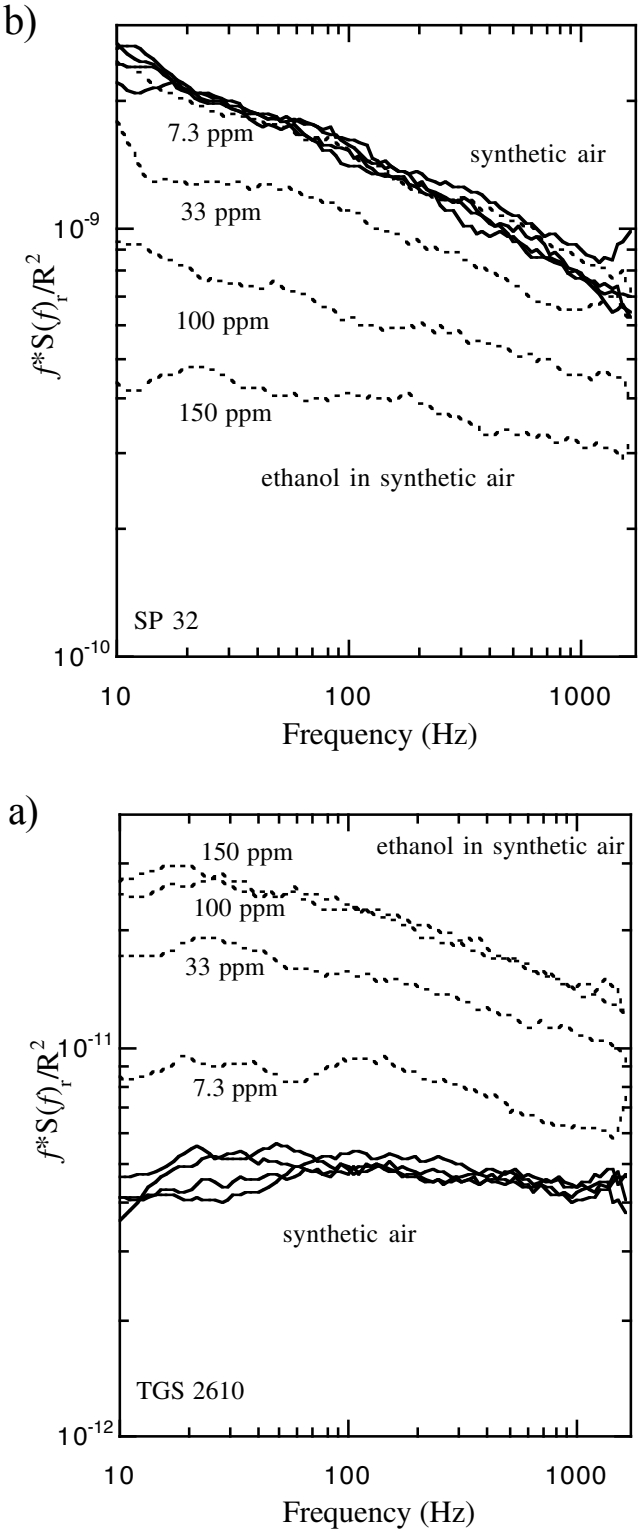

Fig. 4. *Normalized spectra multiplied by the frequency measured in synthetic air (solid lines), and 7.3 ppm, 33 ppm, 100 ppm and 150 ppm of ethanol in synthetic air (doted lines) for (a) TGS 2610 and (b) SP 32 sensors.*

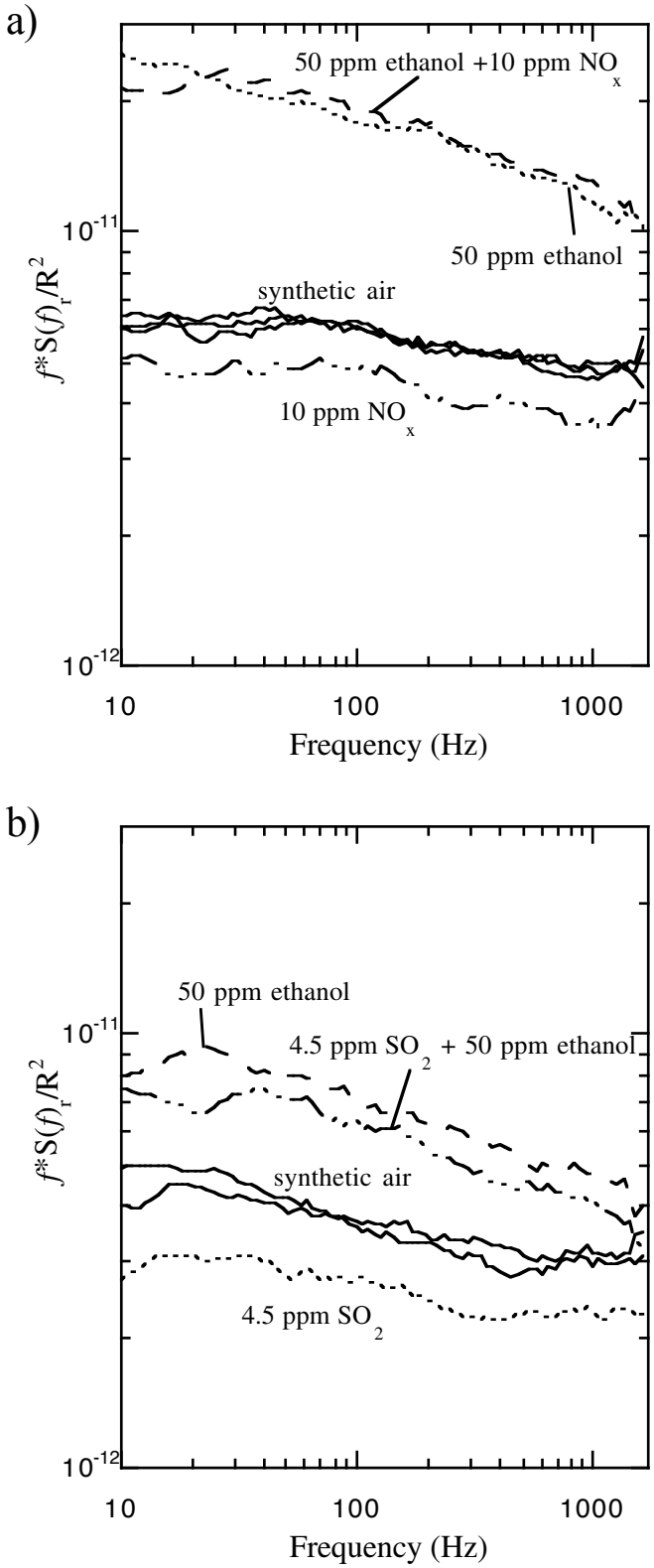

Fig. 5. *Normalized spectra multiplied by the frequency measured for TGS 2610 during the exposure to (a) synthetic air (solid lines), 10 ppm of NO_x in synthetic air (dashed and doted line), 50 ppm of ethanol in synthetic air (doted line) and their mixture in synthetic air (dashed line), and to (b) synthetic air (solid lines), 4.5 ppm of SO_2 in synthetic air (doted line), 50 ppm of ethanol in synthetic air (dashed line) and their mixture in synthetic air (dashed and doted line).*

4. Summary

It is shown that the exposure to different gases in synthetic air causes reproducible variations in the power spectral density of the resistance fluctuations. The results show that there is a potential to identify gases in atmosphere using only one sensor through analysis of the stochastic signal component.

It is remarkable that, in the case of several different sensors, sensing and identification of various gases, which are different from the gas for which the sensors were designed, is possible with the stochastic sensing method.

However, the various behaviors observed in the different commercial sensors indicated that a thorough study of the response of different sensors and sensor materials is still needed before the technical application of the method.

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