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Surface diffusion enhanced chemical sensing by surface acoustic waves

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Abstract

A new chemical sensing method that enhances sensitivity and selectivity is proposed and verified by theoretical analysis. This method is based on the spectral analysis of the dynamics of adsorbed molecules on surface acoustic wave (SAW) delay lines and resonators. Various sources of noise, including diffusion and adsorption–desorption noise is considered.

Keywords: Multiple gas sensing; Analysis of gas mixtures; High sensitivity and selectivity; Fluctuations; Adsorption–desorption noise

1. Introduction

In a recent paper [1], we have proposed a new way of processing the stochastic component of signals in chemical sensing surface acoustic wave (SAW) devices. The present conference paper is an expanded version of that theoretical study, where adsorption–desorption fluctuations have also been included.

Homeland defense, including anti-terrorist efforts, require highly selective, sensitive, and reliable detection of harmful agents. Intensive research has been going on to use chemical and biological sensor elements [1,2] to develop systems known as electronic noses, for gas and odor sensing, and electronic tongues, for fluid sensing.

Presently available electronic noses and tongues, mostly based on the measurement of conductance or electrochemical potential in surface-active devices, are neither reliable, nor sufficiently selective or highly sensitive [1,2]. The sensor components have a high false alarm rate, short lifetime, and they deteriorate relatively fast.

A more sensitive and reliable way of gas sensing is based on SAW devices [3–5]. In Fig. 1, the outline of a SAW delay line applied for gas sensing is shown, with the two electrode pairs A and B, and the adsorbed gas molecules. The extra inertial mass of the adsorbed molecules decreases the propagation velocity of the SAW, thus the delay time increase between A and B is approximately proportional to the number of adsorbed molecules in the sensing zone (a.k.a. sweetspot) between the electrode pairs.

Fig. 2 shows the outline of a gas sensing SAW delay line in an oscillator based measurement circuit. The bandpass filter selects a single oscillatory mode and the oscillation frequency is measured by the frequency counter.

In SAW gas sensing devices, ppb gas concentration and nanogram adsorbed mass detection sensitivities have been demonstrated [3,4], and orders of magnitude greater sensitivity is predicted for oscillation frequency around GHz and higher. On the other hand, the selectivity of traditional SAW gas sensor devices is very poor; SAW sensors measure the total mass of the adsorbed gas molecules irrespectively of their kind. Selectivity can be somewhat improved by using appropriate sensing films.

In this paper, we propose a new way of SAW gas sensing. The new method is based on the spectral analysis of measured frequency fluctuations in the SAW device. This fluctuation-enhanced sensing is not only more sensitive than the classical methods but also, it gives quantitative information about the kind of adsorbed gases. Moreover, we demonstrate that the new method provides a quantitative analysis of the composition of a gas mixture even when using a single SAW device.

2. Diffusion noise

The gas molecules adsorbed on the surface execute a surface diffusion process, which is essentially a random walk over the entire surface of the SAW device. Assume that

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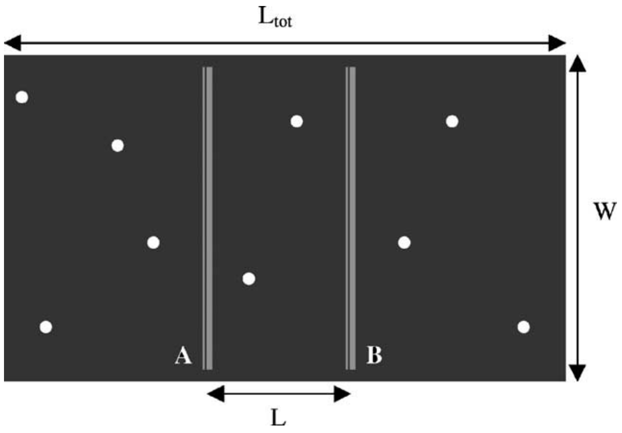

Fig. 1. The surface acoustic wave delay line with the electrodes and the adsorbed molecules [1]. The delay time increment between the two electrode pairs will be proportional to the number of adsorbed molecules in the sensing zone (a.k.a. sweetspot) between the electrodes. The part outside the sweetspot usually contains wave absorbent coating to avoid interference from the walls.

the SAW device has a thin, uniform coating over the whole surface so that the diffusion coefficient D of the adsorbed gas molecules is constant all along the surface, including the electrode range, see Fig. 1. Due to the independent random walking of each molecule, the instantaneous number $N(t)$ of molecules over the sweetspot is fluctuating. Therefore, the SAW oscillator arrangement shown in Fig. 2 will have spontaneous fluctuations of the oscillation frequency f_{osc} and the instantaneous value $\Delta f_{osc}(t)$ of the frequency deviation from the frequency of the gas molecule-free case will be proportional to $N(t)$. The dynamical properties of the fluctuation $N(t)$ and the induced frequency fluctuations $\Delta f_{osc}(t)$ will be determined by the value of D and the geometry of the SAW device and the sweetspot.

The low-frequency power density spectrum (noise spectrum) S of the ac component of $\Delta f_{osc}(t)$ is described by the diffusion noise theory of MacFarlane [6] and Burgess [7] which, due to the linear coupling between $N(t)$ and $\Delta f_{osc}(t)$, can directly be applied here [1]:

$$S(\omega) = N_{tot}\frac{KL^2}{D\Theta^3}[1-(\cos\Theta+\sin\Theta)\exp(-\Theta)]^2, \tag{1}$$

where N_{tot} is the total number of gas molecules adsorbed on the surface, K a constant characterizing the time average $\langle\Delta f_{osc}(t)\rangle_t^2$ of the frequency shift due to a single molecule, and L the length of the sweetspot, see Fig. 1:

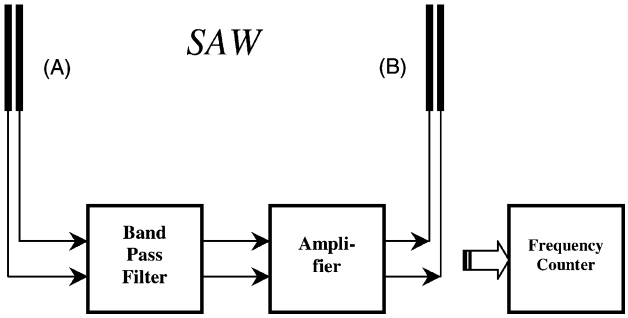

Fig. 2. Outline of a gas sensing SAW delay line in an oscillator based measurement circuit [1]. The bandpass filter selects a single oscillatory mode and the frequency is measured by the frequency counter.

$$\Theta = L\sqrt{\frac{\omega}{2D}}; \tag{2}$$

and the angular frequency $\omega = 2\pi f$ [1].

Eq. (1) is valid only if the fluctuation has one-dimensional origin, which means that the width W and the length L of the sweetspot satisfy the following relations [1]:

$$L_{tot} \gg L \tag{3}$$

and

$$W \gg L, \tag{4}$$

where L_{tot} is the total length of the SAW device [1].

The interesting feature of Eq. (1) is that the spectrum has two different frequency regimes and, in both regimes, it follows a power-law scaling:

$$\begin{aligned} &S(f) \propto f^{-0.5} \quad (\text{for } \Theta \ll 1),\\ &S(f) \propto f^{-1.5} \quad (\text{for } \Theta \gg 1). \end{aligned} \tag{5}$$

The crossover frequency between the two regimes is given as [1]

$$\Theta = L\sqrt{\frac{\omega_c}{2D}} \cong 1, \quad \text{or} \quad f_c \cong \frac{1}{\pi}\frac{D}{L^2}. \tag{6}$$

From the theory of diffusive fluctuations, Eq. (1) and relation (5) is valid even if there is only a single molecule on the surface, $N_{tot} = 1$. On the other hand, when the surface contains several gas molecules with different diffusion coefficients, the total spectrum will be the sum of the corresponding spectra of the different gases:

$$S(f) = N_1 S(f, D_1) + N_2 S(f, D_2) + \cdots. \tag{7}$$

3. Fluctuation-enhanced sensing

Fluctuation-enhanced sensing means the statistical analysis of the dynamics of the measured frequency fluctuations of the SAW based oscillator device, see Fig. 3. In this paper, we make use of the power density spectrum $S(f)$ of the ac component of the frequency fluctuations. The measured $S(f)$ spectrum is described by Eqs. (1), (2) and (7), for the case when relations (3) and (4) hold. Relations (3) and (4) are easy to satisfy by the design of the geometry of SAW device. Using the measured $S(f)$ implies strongly enhanced selectivity and sensitivity [1], as we will shown in the following paragraphs.

One of the factors contributing to increased sensitivity of fluctuation-enhanced sensing is the greatly reduced temperature dependence. The drift of the frequency f_{osc} due to temperature variations is the dominant limit of the resolution and accuracy of traditional SAW gas sensors [3,4].

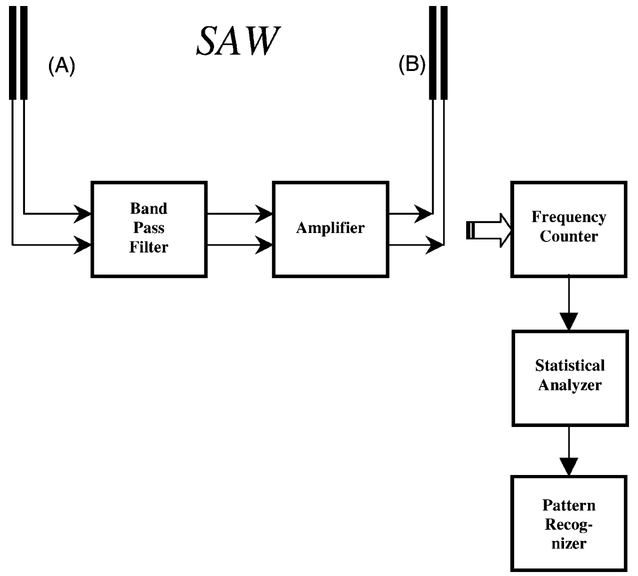

Fig. 3. Fluctuation-enhanced gas sensing [1]. The output of the frequency counter is fed into a statistical analyzer, which can be a spectrum analyzer or a more advanced instrument. It may measure other characteristics, such as amplitude distribution of the fluctuations. The pattern recognizer identifies the generated pattern.

In fluctuation-enhanced sensing we are interested in $S(f)$ which is related to the ac component of the frequency fluctuations only, thus the temperature dependence, causing a slow dc drift, is significantly reduced [1].

Another important factor contributing to higher sensitivity is the fact that, due to the particular shape of the frequency spectra of diffusion processes, the diffusion noise can be easily distinguished from other sensor noise processes, such as adsorption–desorption, and thermal noise [5]. Adsorption–desorption noise itself can be used to access chemical information, see following paragraphs.

The strongly enhanced selectivity stems from the fact that the $S(f)$ is a pattern, not a single number. Therefore, not only the strength of $S(f)$ has information about the adsorbed gas molecules but also its shape. While in the case of classical SAW gas sensing the only information we obtain is the total adsorbed gas mass, fluctuation-enhanced SAW sensing is able to analyze not only the total adsorbed gas mass but also the diffusion coefficients of the gas, for example by Eq. (6). In the case of a gas mixture, the composition of the mixture can be analyzed by using Eq. (7). In conclusion, a single sensor can be used as a complete electronic nose.

Fluctuation-enhanced gas sensing has the potential to replace more expensive analytical methods, such as gas chromatography, by this portable, less expensive way of sensing devices.

4. Diffusive spectra and their combination

In this section, we demonstrate the efficiency of fluctuation-enhanced SAW sensing of gases. The demonstration is based on practical data and analytical calculations for the cases of single gas and a gas mixture.

Defect diffusion in the bulk of solids is a slow process and its activation energy is in the range of 0.1–1 eV. Surface diffusion processes are known to be much faster and their activation energy therefore much smaller.

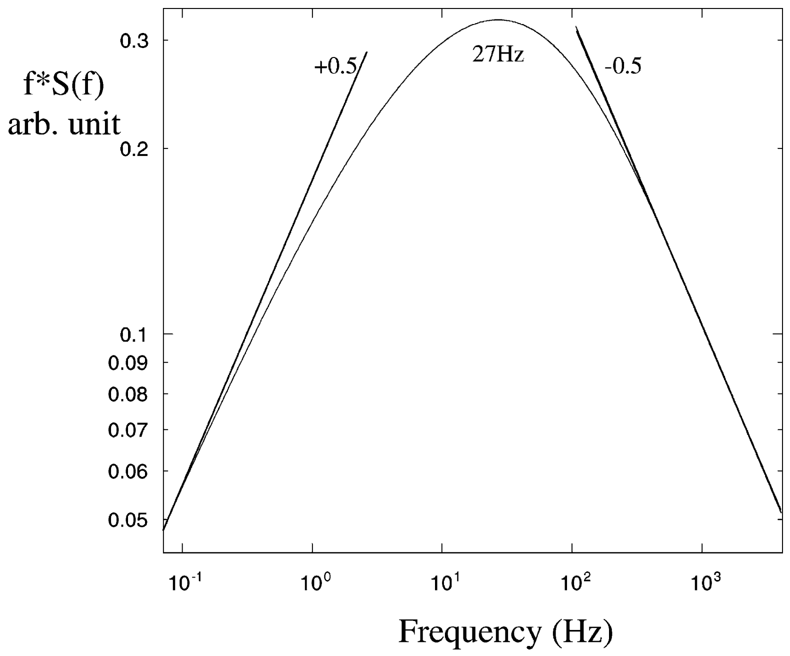

Fig. 4. Response in the case of a single agent [1], for $L = 0.1$ mm, $E = 0.1$ eV, $d = 0.3$ nm, $T = 400$ K, $f_0 = 2 \times 10^{14}$. The spectrum is multiplied by the frequency for the better visibility of the crossover point. The obtained curve, which is plotted on a log–log scale, converges to a slope of 0.5 in the low-frequency limit and -0.5 in the high-frequency limit.

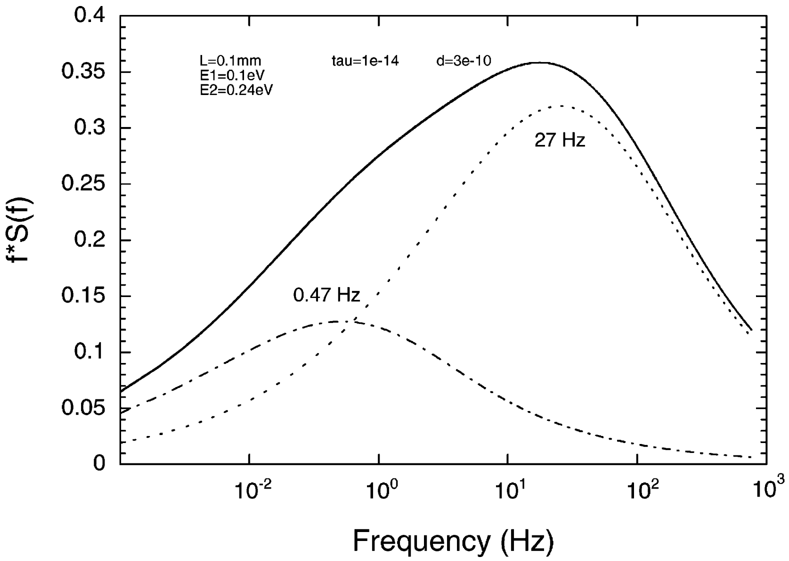

Fig. 5. Response in the case of two different agents with different diffusion activation energies [1]. $L = 0.1$ mm, $E_1 = 0.1$ eV, $E_2 = 0.245$ eV, $d = 0.3$ nm, $T = 400$ K, $f_0 = 2 \times 10^{14}$. The two dashed curves show the independent spectral contributions of individual agents. The measured (solid) curve is the sum of these curves. By using two-component analysis, and the known shape for a single agent, the curves can be reconstructed from the sum.

For the estimation of the diffusion coefficient, we used the following well-known equations:

$$D = d^2 f_s, \tag{8}$$

where d is the mean random walk step size (typically ≈ the lattice constant) and f_s is the mean frequency of steps, which can be given as

$$f_s = f_0 \exp\left[-\frac{E}{kT}\right], \tag{9}$$

where f_0 is the mean attempt frequency, E the activation energy of surface diffusion, k the Boltzmann constant and T is the absolute temperature.

In Fig. 4, the $f \times S(f)$ pattern is shown in the case of a single agent with activation energy $E = 0.1$ eV, for sweet-spot length $L = 0.1$ mm, $d = 0.3$ nm, $T = 400$ K and $f_0 = 2 \times 10^{14}$. The crossover frequency is at 27 Hz. From the measurement of this crossover frequency, the diffusion coefficient D of the gas can be determined so the gas can be identified. Note that the obtained curve, which is plotted on a log–log scale, converges to a slope of 0.5 in the low-frequency limit and −0.5 in the high-frequency limit.

Fig. 5 shows the $f \times S(f)$ pattern in the case of two different gases with different activation energies $E_1 = 0.1$ eV, $E_2 = 0.245$ eV, for $L = 0.1$ mm, $d = 0.3$ nm, $T = 400$ K, $f_0 = 2 \times 10^{14}$. The two dashed curves show the independent spectral contribution of the different agents. The measured (solid) curve is the sum of these two curves. By using Eq. (7) and the known shape for a single agent, the dashed curves can be reconstructed by two-component analysis from the measured sum and the gases can be identified. After calibrating the sensor for different gases and gas concentrations, the dashed curves can be used for quantitative analysis of gas mixtures.

5. Adsorption–desorption noise

So far, we have assumed that the diffusion time τ_L is much shorter than the characteristic adsorption–desorption time constant τ_{ad}:

$$\frac{L^2}{D} = \tau_L \ll \tau_{ad} = \frac{\tau_a \tau_d}{\tau_a + \tau_d}, \tag{10}$$

where τ_a and τ_d are the adsorption and desorption time constants, respectively. The random nature of adsorption–desorption process is causing fluctuations of the mass of adsorbed vapor [5]. Then, the resulting power spectrum of fluctuations of SAW frequency have a Lorentzian spectrum:

$$S(f) \propto \frac{1}{1 + 4\pi^2 f^2 \tau_{ad}^2}. \tag{11}$$

This fluctuation is invisible if condition (10) holds. However, in the opposite case:

$$\frac{L^2}{D} = \tau_L \gg \tau_{ad} = \frac{\tau_a \tau_d}{\tau_a + \tau_d}, \tag{12}$$

the fluctuation spectrum given by Eq. (11) will dominate. As τ_{ad} is characteristic of the bounding interaction between agent and the surface, the measured spectrum (11) can also be used to identify various agents using the same technique described in the previous section.

6. Conclusion

We introduced fluctuation-enhanced gas sensing by SAW devices and demonstrated its superior sensitivity and selectivity for the detection and identification of gases and quantitative analysis of gas mixtures.

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Biographies

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