Combinatorial Molecule Counting by Fluctuation-Enhanced SAW and MOSFET Sensors

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ABSTRACT

A new method for the detection and identification of gas molecules and the analysis of their mixtures is proposed. The new process is based on the analysis of the amplitude density function of surface acoustic wave resonator (SAWR) or MOSFET signal(s). The proposed method has the potential to detect and identify very small numbers of molecules, even a single one. When the number of adsorbed molecules is small, the exact number and type can be determined from first principles of combinatorics.

Keywords: Calibration by first principles, binoninal distribution, molecule detection, SAW, noise, standards, metrology

1. INTRODUCTION

Fluctuation-enhanced chemical sensing has the attractive capability of detecting and analyzing complex chemical mixtures by using a single sensor. This characteristic has the strongest application potential for Surface Acoustical Wave (SAW) devices or MOSFET sensors. SAW devices are relevant due to the expensive and extensive hardware needed for each device. MOSFETs are relevant due to the same kind of geometry and the even higher sensitivity. Unlike artificial noses with Taguchi sensors, it is not feasible to use many different SAW sensors working parallel in an electronic nose for complex analysis. In this paper, we will consider SAW devices as an example, however most of the arguments apply to MOSFET based sensors as well.

SAW-based fluctuation-enhanced chemical sensing is using the stochastic component of the sensor signal to extract the surface diffusion coefficient of the adsorbed gas molecules and both it’s working principle and efficiency are reminiscent of chromatography, though it is a much more cost-effective and compact solution of the task. In Figure 1, the general scheme of fluctuation-enhanced sensing with a SAW is shown. In a recently published study, as an example, the power density spectrum, $S(f)$, of the sensor signal was evaluated by the statistical analyzer. It was pointed out that 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. In the case of a gas mixture, the composition can be analyzed by multi-component analysis, thus a single sensor can be used as a complete electronic nose.

Figure 1. Fluctuation-enhanced gas sensing. The output of the Frequency Counter is fed into a Statistical Analyzer, which can be a spectrum analyzer or a more advanced system. It may measure other characteristics, such as amplitude distribution of the fluctuations. The Pattern Recognizer identifies the generated pattern.

In the present paper, we propose an improved method of statistical analysis which includes not only the time-dependent dynamics but also the amplitude distribution. By using these tools, the fluctuation-enhanced sensing is approaching it’s full potential and indicates standalone properties.

The amplitude density function contains information about the system parameters. This information can be extracted by comparing the measured and the theoretical density functions. In this work we propose to determine the number of adsorbed molecules using this method.

2. THE SPECIAL PURPOSE SENSOR DESIGN

The combinatorial fluctuation-enhanced sensing needs at least two different zones on the sensor where the adsorbed molecules can diffuse freely, see Figure 2. The diffusion takes place within the zones and the particles can freely move from one region to the other. The space occupied by the two zones is surrounded by a diffusion barrier that limits the diffusion to these regions. The asymmetric arrangement, see Figure 2 (a), consists of an active zone (a.k.a. sweet-spot) A and a passive zone P. The symmetric arrangement consists of two active zones A1 and A2, respectively. The SAW electronics is continuously monitoring the instantaneous number of molecules in the active zone(s). In the case of the asymmetric arrangement, the instantaneous amplitude of the output signal at the output of SAW electronics, which is at the output of the frequency counter, is:

\[ U_{\text{out}}(t) = KN_A(t) \] (1)
where $K$ is a calibration constant and $N_A(t)$ is the instantaneous number of molecules in the active zone $A$.

In the case of the symmetric arrangement, we have two correlated output signals with instantaneous amplitudes:

$$U_1(t) = KN_1(t) \quad U_2(t) = KN_2(t)$$

where $K$ is a calibration constant and $N_1(t)$ and $N_2(t)$ are the instantaneous numbers of molecules in active zones $A_1$ and $A_2$, respectively.

If the sweet–spot and the complementary spaces $A$ and $P$, and $A_1$ and $A_2$, respectively have the same size (symmetric geometry), then the signal will be a symmetric square wave. As the symmetric square wave has the greatest fluctuation power, this geometry is the preferred one.

In the present paper, we focus our interest on the asymmetric arrangement that is a simpler and thus less expensive implementation. However, we shall point out some of the advantages of the symmetric solution.

Our main goal is to show that the amplitude distribution of the signal, in the case of small number of molecules, serves as a tool for single molecule detection and first-principle calibration of the device.

### 3. MOLECULE COUNTING

The adsorbed gas molecules execute a surface diffusion process, which can be modeled as a two dimensional random walk over the entire surface of the SAW device, provided that the adsorbed agent molecules do not interact with each other. In this section we outline our method for sensors with one active zone. We assume that we detect only one type of molecules and that the characteristic diffusion time $\tau_L$ is much shorter than the characteristic adsorption-desorption time constant $\tau_{ad}$

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

(Figure 2. Simplified diagrams of combinatorial fluctuation-enhanced SAW sensors. Asymmetric arrangement (a) and symmetric arrangement (b).)

In the case of the symmetric arrangement, we have two correlated output signals with instantaneous amplitudes:

$$U_1(t) = KN_1(t) \quad U_2(t) = KN_2(t)$$

where $K$ is a calibration constant and $N_1(t)$ and $N_2(t)$ are the instantaneous numbers of molecules in active zones $A_1$ and $A_2$, respectively.
where \( L \) is the length of the sensor surface, \( D \) is the diffusion coefficient of the adsorbed molecules, \( \tau_a \) and \( \tau_d \) are the adsorption and desorption time constants, respectively. The latter condition can be relaxed if the sensor has two active zones; the adsorption-desorption noise can be suppressed by using cross-correlation analysis of the two outputs.

The probability of a molecule residing in a region is proportional to the area of the region in question. Let \( p = \frac{\mu_{\text{active}}}{\mu_{\text{total}}} \) the ratio of the active zone and the total surface area of the sensor. Then the probability density of the molecule distribution is approximated by

\[
P(r, n) = \frac{n!}{r!(n-r)!} p^r (1-p)^{n-r}, \quad 0 \leq r \leq n \tag{4}
\]

where \( r \) is the number of molecules in the active region and \( n \) is the total number of agent molecules on the sensor. Figure 3 shows \( P(r, n) \) for \( n = 1, 2, \text{ and } 5 \).

![Figure 3](image)

**Figure 3.** Theoretical density function \( P(r) \) for equal active and passive area and for varying number of adsorbed molecules: (a) \( n = 1 \), (b) \( n = 2 \), (c) \( n = 5 \).

Since the measured voltage \( U \) is proportional to the number of molecules in the active zone, the normalized amplitude density (histogram) \( P(U_i) \) of the measured \( U_i \) time series will approximate the above density function. Figure 4 depicts numerically simulated experimental density functions corresponding to the theoretical densities shown in Figure 3. The number of adsorbed molecules, \( n \), can be estimated by comparing the measured density function with \( P(r, n) \) for various values of \( n \).

So far we assumed that we are detecting a single agent, i.e. the adsorbed molecules are all of the same type. A similar process can be used for a mixture of molecules provided that the number of adsorbed molecules is small and the calibration constants \( K_j \) of different type of molecules are sufficiently separated. The theoretical density function can be calculated as the convolution of the individual densities for the molecule types in question.
Figure 4. Numerically generated experimental densities for equal active and passive area and for varying number of adsorbed molecules: (a) \(n=1\), (b) \(n=2\), (c) \(n=5\). The vertical axes have linear scale for the quantity \(P(U)\).

Concerning the possible technical realization of molecule counting or first-principle calibration of the device, it will require a very small measuring surface in order to keep the number of adsorbed molecules small; to have only a few molecules on the surface. MOSFET devices of such small size are easier to manufacture than SAW devices.

**CONCLUSION**

We have proposed a new chemical sensing method that can be used for molecule counting and for first-principle calibration of SAW and MOSFET sensing devices.

**REFERENCES**