Thin nanocrystalline semiconductor films as selective chemical sensors for ammonia, acetone and other donors

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Abstract. Studied are the films of variously doped polycrystalline n-semiconductors (ZnO, SnO$_2$) as selective sensitive elements (SE) of chemical sensors for various gases and vapours (ammonia, acetone, propane, ethanol, hexane, solvent, turpentine etc.) in artificial air. It has been revealed that their conductivity changes under temperature modulation makes possible data processing which identifies the impurities above. This processing is based on nonlinear regression estimation of so called principal parameters which set is unique for every concentration of every of the gases/vapours.

1. Introduction

Nanocrystalline wide gaped semiconductors are well known as most promised materials for artificial olfaction, so called e-nose assigned for monitoring of different impurities in air or another gas-carrier. Due to huge specific area ($m^2/g$) and small crystallite size compared or even less of Debye length their resistance is extremely sensitive to particles chemisorption accompanied by ionization with injection/trapping of zone carriers. Usage of working temperature modulation [1] of the SE gave more rich information compared with fixed temperature conductance $\Delta\sigma, \mu S$ measurements when the responses are similar as a rule for all particles of donor/acceptor type. This informativeness provides success for sophisticated methods of data processing including regression procedures [2], neural networks, artificial intellect at all. In present work authors present new method of processing the $\Delta\sigma, \mu S$ signals recorded in temperature modulation mode which is based on essentially nonlinear regression estimation. The method enables reliable identification various reducing impurities in air such as ammonia, acetone, ethanol, hexane, propane etc.

2. SE fabrication

Tin dioxide was received [2] by hydrolysis of tin sulfate (IV) into meta-tin acid (H$_2$SnO$_3$) followed with heat dehydration to Sn$_{1+x}$O$_2$ powder with ultra-stoichiometric metal atoms acting as electron donors. For catalyst doping with palladium PdCl$_2$ solution was added to the powder which reduced then by sodium formate (HCOONa) with formation of 2 — 5 nm size catalytic Pd-clusters on SnO$_2$ grain surface (figure 1). The mass was washed thoroughly in distillated water then dried at 60°C mixed with organic binding and the paste was deposited on melted quartz substrate supplied with Pt-contacts and inner Pt-heater [ibid] providing heating from 20°C to 500°C during 1 s. Thus fabricated SE was dried at 150°C and sintered at 720°C.
The ZnO films were fabricated by mechanical and thermal treating the mixture of zinc acetate dihydrate \((\text{CH}_3\text{COO})_2\text{Zn}\cdot2\text{H}_2\text{O}\), 2-methoxyethanol \(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}\) and 2-aminoethanol \(\text{HOCH}_2\text{CH}_2\text{NH}_2\).

3. Experimental setup
There was used commercial device Mikrogas-FM12 produced by Delta-C Ltd., Moscow (http://deltagaz.ru/) which provides multiple dynamical attenuation of the substances studied to gain ppm-range concentrations of impurities in flow from clean air generator. An average relative accuracy of the concentration value was of about 4%. The temperature of the flow was maintained constant at room level though this parameter of the sensitive layer varied from about 100 to 500°C. As for ethanol and propane it enabled minimal concentrations on entry of about \(10^{-3}\) vol.%. For ammonia this limit was of order 0.1 mg/m³, for acetone it was 19 mg/m³ and for hexane 7 mg/m³. These values are much less than correspondent threshold limit levels (TLV) or lower explosive limits (LEL).

![Figure 1. JEOL JSM 6400 SEM image of SnO₂-PdO film. Green dots are Pd-clusters.](image1)

![Figure 2. Reproducibility of heating regime at measurements with various concentrations of NH₃ in air.](image2)

4. Measurements
As been noticed above the temperature modulation was used to obtain the responses of SE DC conductance change \(\Delta\sigma,\mu\text{S}\) for elevating temperature \(t,^\circ\text{C}\) in air with analyte with respect to the value \(\sigma_{\text{air}}(t_{\text{low}})\) in clean air at initial temperature \(t_{\text{low}},^\circ\text{C}\). Opposite to cyclic modulation [2,3] only short time (\(\tau\approx1.5\) s) heating phase was used to record the \(\Delta\sigma\)-changes. Therefore, both measurement time and SE exploiting wear were less than that for long time multiple cycling. The measurements were fulfilled in non-stationary mode because the “saw”-time of about \(\tau\) was not sufficient for establishing thermodynamic quasi-equilibrium between gas phase and adsorbed particles and semiconductor in wide range of quickly growing temperatures.

The physical temperature range itself \([T_{\text{min}},T_{\text{max}}]\) had been chosen to include all signal peculiarities and to overwhelm all temperature intervals for data proceeding for every pair SE—analyte. As for heating regime \(t'(t,\text{ms})\) it was elaborated to be highly reproducible with accuracy \(\pm0.5\) deg for the temperature “saw” so all the curves merged into one (figure 2). For some pairs SE—analyte (SnO₂ — acetone/hexane/..) the physical range was [433K, 768K] and for others (ZnO—ethanol) respectively [369K, 723K].

This high reproducibility of TM regime and \(\Delta\sigma(t/\text{ms})\) recording grid along with stability of analyte concentration in air flow and also its temperature all these made it possible registration highly smooth curves for the conductance change. Therefore, the argument time \(t/\text{ms}\) was substituted by reciprocal current absolute temperature of the SE, i.e. \(z=1000/T,\ \text{K}^{-1}\). So the responses were treated and
processed in more physical representation as $\Delta \sigma(1000/T)$. All this allowed in its turn data processing of $\Delta \sigma$—signal in terms of nonlinear estimation with extremely high Student’s criteria for the parameters determined.

5. Data processing

Main objective of this proceeding was to detect and properly describe not viewed visually distinctions between the $\Delta \sigma$ responses for different analytes in wide range of concentrations. Of course, if two substances each in its own concentration give yet absolutely identical curves $\Delta \sigma(1000/T)$ we’ll never distinguish them by all conductometric means. However, this situation is rather unlikely for most required substances. So, the problem the authors tackled was to distinguish analytically, i.e. in terms of numeric values the curves that may look out very similar one another but differ in their mathematical qualities and quantities and not only in the peculiarities above.

This was rather general mathematical problem which the authors have solved at significant extent by means of mathematical statistics in frames of nonlinear regression method based on Levenberg — Markwardt (damped least square— DLS) algorithm [4]. Due to the method every time/temperature series $\Delta \sigma(1000/T(i))$ should be interpolated by model parametrized function to estimate its parameters. These functions should be chosen relatively simple, say, rational ones, and their parameters should be responsible for analyte concentration and kinetics peculiarities or absence of these ones. So, there were used following algebraic functions:

$$F_1(z) = \frac{A_1}{z^4 + b_1z^3 + c_1z^2 + d_1z + h_1}, F_2(z) = zF_1(z), F_3(z) = \frac{A_2}{z^4 + b_2z^3 + c_2z^2 + d_2z + h_2},$$

$$F_4(z) = \frac{A_3}{b_3z^4 + c_3z^3 + d_3z^2 + h_3z + 1}, F_5(z) = \frac{A_4}{b_4z^3 + c_4z^2 + d_4z + 1} \quad (1) - (6).$$

The principal parameters $A_1, A_2, A_3, A_4, A_5, A_6$ in numerators of (1)—(6) are to be positive ones for they are assigned to be responsible for signal “power”, i.e. analyte concentration $C$ (mg/m$^3$, vol.%., ppm, etc.). And the secondary ones, i.e. $b_i, c_i, d_i, h_i$ in denominators are to define the peculiarities of the kinetics $\Delta \sigma(1000/T)$, i.e. extremums, bending points etc. (figure 3).

![Figure 3. Different type $\Delta \sigma(1000/T)$-responses for various analytes in air on ZnO-based SE.](image)

For every pair “SE—analyte” all these principal parameters were estimated with the use of StatSoft Statistica 14 at many concentrations $C$ in actual range including TLV- and 0.1 of LEL-levels. The values of $A_1, A_2, A_6$ were considered as significant ones if and only if all the rest parameters in formula
were also estimated on confidence level of \( P=0.95 \) (\( \alpha=1-P=0.05 \)). This fact guaranteed sufficiently high levels of Student’s criteria for the principal parameters and hence smooth enough gauge curves \( A_i(C) \) on so called selectivity or gauge portrait of the pair.

**Figure 4.** Identification of TLV ammonia by the \( \text{NH}_3 \)-on-ZnO gauge portrait by equal abscissas.

This gauge portrait was formed by all plots in logarithmic coordinates \( \ln A_i(\ln C) \), \( i=1—6 \) which points had been estimated significantly in whole set. Some of them may have gap over certain \( C \)-interval where confidence level of one or more of the coefficients in corresponding formula occurred less the 95 % (figures 4 — 6).

**Figure 5.** Solvent vapours’ identification by solvent-on-SnO\(_2\)-gauge portrait.

**Figure 6.** Non identification of 0.083 vol.% propane as acetone by the acetone-on-ZnO-gauge portrait.

The portrait thus built serves as identification tool for analyte in air. Namely, if the set of parameters estimated fit the portrait, i.e. the level lines \( A_{iX} \) for analyte \( X \) intersect their gauge plots
$A_1(C)$ built for the analyte $Y$ in points with approximately equal abscissas $C^*$ (figure 4) then the $X$ is $Y$ and $C^*$ is its concentration in the portrait units.

On the contrary, if the abscissas differ from each other or some parameter $A_i$ is not estimated for the $X$- or $Y$-analytes or there is no intersection point then $X$ is not $Y$ (figure 6). In this case non-identification, we should try another one of gauge portraits available.

Among the curves $A_i(C)$ there should be monotonic ones in actual $C$-range or having a pronounced growing trend though with inevitable fluctuations. Along with good continuity and smoothness the curve should have steep slope and hence significant total variation on this actual interval even when been plotted in logarithmic coordinates ($\lg A_i(C)$, figure 4). After identification of the analyte this curve may serve as additional measuring tool for more precise determination of the concentration and evaluation of its accuracy. This was also fulfilled by means of nonlinear regression as interpolating of the dependence $C(A_i)$ by calibration formula.

These calibration curves were used on intervals of their steep slope and thus define the concentration subranges. When the point drops from one subrange it should appear in another one with different gauge formula. Though these subranges may have common part where both two formulas work simultaneously and estimate the concentration more reliably.

As a rule, the gauge formulas were essentially nonlinear. Thus for ammonia in air on ZnO based SE this was as follows $C(A_3) = W \cdot A_3^{n+0.001} \frac{f_5}{A_5}$ (figure 7). This formula worked well providing good accuracy of about 5 % and giving random independent residuals distributed due to normal law. Everything had been proved by Statistica 14 program. However, for propane in air on the same ZnO-SE there were received almost ideal proportional dependences $C(A_3)$ (figure 8). This prominent case provided sure to link this parameter with physical value of chemisorbed analyte and thus to make it as one more indirect tool for studying propane chemisorption on ZnO. In fact, this is highly unlikely that the proportionality has appeared as a result of mutual annihilating of all the nonlinearities may arise by this temperature modulation experiment.

![Figure 7](image1.png)  ![Figure 8](image2.png)

**Figure 7.** Nonlinear gauge plot of concentration $C$ vs $A_3$ with residuals for ammonia in air on ZnO-SE.

**Figure 8.** Ideal proportional gauge curve $C(A_3)$ for propane in air on ZnO-based sensor.

6. **Optimization of temperature interval**

To receive visually continuous and smooth plots $A_i(C)$ the nonlinear estimations due to (1)–(6) are to give as high as it possible the Student’s criteria $t(A_i)$. It means that temperature range for one principal parameter may differ from that for another. From other hand, to determine precisely concentration via
the plot $A_i(C)$ it should be characterized by a significant variation and hence steady steep slope seen well in logarithmic coordinates.

This problem was solved numerically by varying the boundaries $T_{min}$ and $T_{max}$ of the interval of signal proceeding. However, physical interval stayed the same and it included all processing intervals. In fact, it was new type optimization problem in which as an objective served not least square value but the $t$-values for principal parameters. This problem was significantly complicated due to essential nonlinearities of the regression formulas (1)–(6) by its coefficients and it created a lot of specific difficulties.

The DLS nonlinear estimation itself had been never considered as simple computational problem because of initial guess (IG) difficulties, possible huge number of iterations, multiple and close to each other solutions etc. To overcome these difficulties an artificial intellect and bioinspired methods were traditionally used. The authors managed to escape the difficulties by formation of data bases for IGs for each pair “sensitive element — analyte”. This was a complicated numerical problem itself because of obvious impossibility for an exhaustive search with any acceptable grid. However, the type of the functions (1)—(6) allowed luckily to solve this problem by simple transformation to linear by the parameters expressions via simple substitution $\Delta \sigma$ by $1/\Delta \sigma$ and recalculation of the coefficients obtained [4]. This procedure initially applied for high concentration of analyte gave the IG for DLS. And the results obtained were used then as next IG for the lower $C$ and so on to ppm-range concentrations.

7. Conclusions
The films investigated and the algorithm above may provide simple, cheap and reliable sensors to identify not only single impurities in air but double ones or even triple [4]. Theoretically, this high selectivity may be further improved through expanding the set of interpolating functions. And implementation of artificial intelligence tools stays a general way in developing e-noses for many applications.

References
[1] Nakata S, Akakabe S, Nakasuji M and Yoshikawa K 1996 Anal. Chem. 68 2067
[2] Shaposhnik A, Moskalev P, Chegereva K, Zviagin A and Vasiliev A 2021 Sens & Act. B 334 129376
[3] Samotaev N, Vasiliev A, Podlepetsky B, Sokolov A and Pisliakov A. 2007 Sens & Act. B 127 242
[4] Chistyakov V, Kazakov S, Grevtsev M and Soloviev S 2021 Tech. Phys. Lett. 47 (3) 275