33.5: New Surface Acoustic Wave Gas Sensor of the Mass-Sensitive Type Sensitive to the Thermal Properties of Gases

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Abstract

The basic principles of a new surface acoustic wave (SAW) gas sensor are described. Being essentially a sensor of the mass-sensitive type, the proposed device possesses certain features of the thermometric SAW sensors and is not only sensitive to the vapors of volatile substances, but capable of detecting gases by their thermal properties as well. This principles consists of making a certain delay of heat fluxes between the substrate of sensitive SAW element (SAW delay line or SAW resonator) and working surface of the sensor's temperature stabilization system. In contrast to the known thermometric SAW sensors, the proposed sensor is characterized by high temperature stability and fast response. A variant of the sensor based on a $LiNbO_3$ SAW delay line with glass spacers between the SAW substrate and is described and some results on detecting propane-butane mixtures are presented, glass spacers being a means providing heat fluxes delay between $LiNbO_3$ substrate and working surface of the sensor's temperature stabilization system.

Keywords

Surface acoustic wave, SAW sensor, mass-sensitive, thermometric, Peltier thermoelectric element, lithium niobate, delay line, heat flux.

INTRODUCTION

Generally devices implementing surface acoustic waves (SAWs) are sensitive to the state of a substrate surface along which the waves are propagating. The adsorption of molecules from the gas phase on the substrate surface produces in particular mass loading of this surface and modifies the SAW propagation parameters, which is reflected by changes in the output signal. This principle is employed in the SAW gas sensors of the mass-sensitive type [1]. In order to provide for a selectivity with respect to the adsorbate, the SAW-guiding surface is coated with a special material exhibiting increased absorption capacity with respect to compounds of one or another class. These gas sensors find increasing application, for example, in the sensor arrays of the modern gas analyzers of the "electronic nose" type [2].

However, the SAW sensors free of the selective coatings offer better reproducibility and stability characteristics [3]. Usually not possessing selectivity, these devices are capable of detecting the vapors of volatile substances adsorbed on the working surface. Such sensors are widely used in the instruments based on portable chromatographs for the detection and recognition of volatile compounds [3], [4].

Modern chromatographs have become universal devices, which requires that the SAW sensors would detect not only the vapors of volatile substances, but the stable and burning gases as well. SAW sensor without sensitive coatings of so called thermometric type [5], [6] could detect these gases.

Such a sensor works as following. SAW delay line or SAW resonator mounted on a special heated plate (constant heat source) is placed inside a measurement chamber. Gas-carrier is flowing through this chamber at a constant flow rate. This heated plate with SAW sensitive device is fixed in the chamber in a certain manner to provide the heat exchange between the plate and the chamber walls mainly through the gas media surrounding this plate. Chamber walls temperature and the temperature of the flowing gas is maintained to be stable and usually essentially lower than that of the heated plate with the SAW sensitive device (constant heat source). Thus the temperature of this heat source will be determined by the thermal properties (temperature conductivity and thermal capacity) and the flow rate of the gas injected into the chamber. The more the thermal properties of the injected gas differ from these of the gas-carrier the bigger the temperature change of the heat source occurring at the injection of the gas under investigation and consequently the better sensor sensitivity. The constant heat source in such a device is usually an electrical heater of the resistive type with stabilized feeding power. SAW device here plays a role of a temperature sensor. Existing SAW sensors of the thermometric type [5], [6] posses rather slow response time, poor temperature stability and can not detect the vapor of volatile organic substances.

SAW sensors of mass-sensitive type usually posses rather good temperature stability rather fast speed of response but using highly effective systems for SAW substrate temperature maintenance [4], [7] such sensors can not detect gases by their thermal properties.

In the present paper we describe the basic principles of a new SAW gas sensor of the mass-sensitive type, which also possesses certain features of the thermometric SAW sensors [5], [6]. As a result, the proposed device is capable of detecting both the vapors of volatile substances and gases by their thermal properties. In contrast to the known thermometric SAW sensors, the new sensor is characterized by high thermal stability and fast response. A variant of the

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sensor based on a 12□0Y–X LiNbO3 SAW delay line is described and some results of the test for detecting propane-butane gas mixtures for household purposes are presented.

THERMOELECTRIC SYSTEM OF SAW SENSOR TEMPERATURE CONTROL

To understand better the operation of suggested new SAW sensor let us first consider the temperature stabilization in SAW sensor of the mass-sensitive type. The temperature stabilization of modern SAW sensors of the mass-sensitive type is provided by using Peltier's thermoelectric elements (TEEs) [4], [7]. Fig.1 shows the typical layout of such a sensor in the measurement chamber [7]. The sensitive sensor element proper is mounted immediately on the TEE working surface. In our case the sensitive element is SAW delay

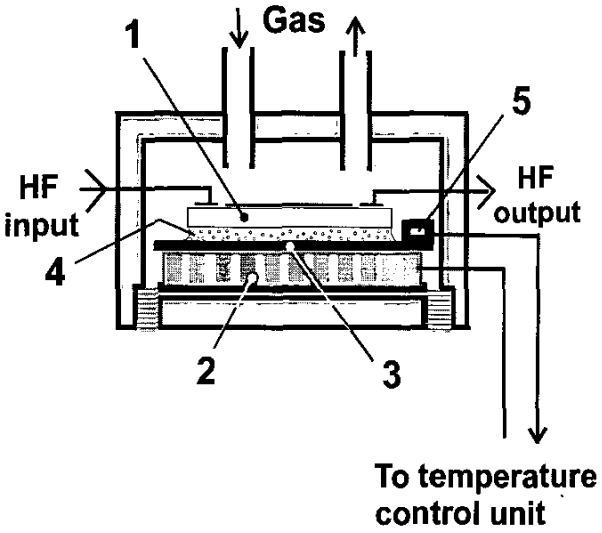

Figure 1. Schematic of SAW sensor inside the measurement chamber. 1-SAW delay line; 2-TEE; 3-working surface of TEE; 4-layer of heat-coducting paste; 5-thermoresistor;

line with the substrate fabricated of 128^0 Y–X $LiNbO_3$ and center frequency of 486 MHz. The substrate dimensions were 0.5 mm x 4 mm x 9 mm. The bottom surface of the SAW sample was adhered with a heat-conducting paste to the working surface of the TEE. The TEE with a temperature sensitive resistor as a temperature sensor on the working face was controlled by a computer providing maintenance of sample temperature in the range 2 – 65 °C with a good stability of ±0.003 °C during at least ten minutes and ±0.01 °C during several hours. The TEE with the SAW sample was mounted inside a metallic housing with corresponding electric leads and gas inlet and outlet.

Temperature stabilization dynamic of the SAW sample was investigated. Phase changes of the SAW delay line output microwave signal caused by two preset TEE working surface temperature changes of 0.5 °C and 1 °C at a maximum rate possible with the temperature stabilization system employed were measured for this purpose. The curve 1 in Fig.2 shows the measurement results of phase change as a function of time at the temperature change of TEE working surface from 57.3 °C to 58.3 °C and the curve 2 shows that at the temperature change from 9.9 °C to 10.4 °C. During these measurements the measurement chamber was placed in a thermostat at 30 °C ± 0.1 °C and the gas-carrier (chromatographic nitrogen) flowed through the chamber. The neasurement results practically did not depend on the flow rate. As can be seen in Fig.2, the SAW substrate temperature is fully established during a time period of ~5 s, the most rapid variation taking place within the first second after the TEE temperature switching.

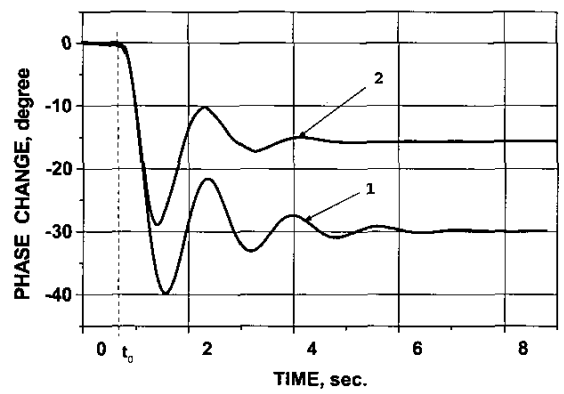

Figure 2. Phase change of the signal taken at the output of the SAW sensor as a function of time at two preset TEE working surface temperature changes. t_0 is the onset moment of the temperature change.

We may suppose that the sensor temperature would return at approximately the same rate to the initial level upon any external thermal action. This action can be produced by the analyzed gas portion admitted to the working chamber, the thermal properties of which (thermal conductivity and heat capacity) may differ from those of the previously flowing gas-carrier.

At a reasonable velocity of the gas flow through the measurement chamber and a reasonable temperature difference between SAW substrate and a gas sample, the external action virtually does not affect the SAW substrate temperature because the temperature stabilization system rapidly compensates for these changes.

The detection of gases by their thermal properties thus requires a certain delay in operation of the temperature stabilization system. Such a delay can be realized, in particular, by retarding the heat flux between the TEE working surface and SAW substrate. For this purpose, we used one or two thin (0.25 mm) glass plates adhered with a heat-conducting paste to the TEE surface, SAW substrate, and to each other. The results of measurements presented in Fig. 3 showed

that a 1^0C change in the TEE working surface temperature is followed by a slower process of attaining

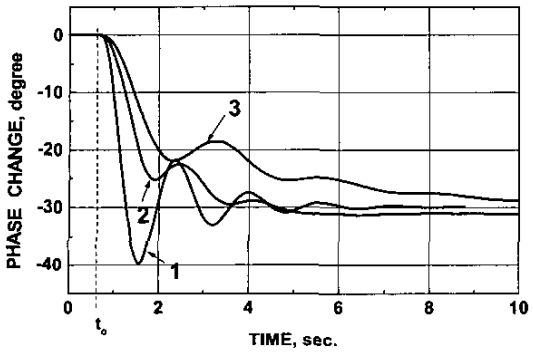

Figure 3. Time variation of the output signal phase in response to a 1 °C change in the TEE working surface temperature (from 57.3^0 to 58.3^0 C, t_0 is the onset moment of the temperature change) for a SAW sensor with different numbers of glass spacers between TEE surface and SAW substrate: curve 1 - no spacers; curve2 - one spacer; curve 3 - two spacers.

the new equilibrium SAW substrate temperature. The greater the number of glass spacers between the TEE working surface and the SAW substrate, the slower the temperature relaxation.

PROPANE -BUTANE DETECTING

Such a modified SAW sensor of the mass-sensitive type with glass spacers between the SAW substrate and TEE working surface was used for detecting a propane-butane mixture by its thermal properties.

A block-diagram of our experimental setup for gas detecting is presented in Fig.4. The measurement chamber (1) (dead volume ≈2 cm^3) with the SAW delay line on the TEE and a metallic capillary pipe for gas supplying were placed in a thermostat (2) at the temperature 30 °C ± 1°C and the stability during several hours not worth than ± 0.1°C. The TEE with special electronic unit (7) and PC was used for SAW sensor temperature control. The main characteristics of this thermo-stabilization system have been described in the previous paragraph of the present paper. A HP Network Analyzer (8) was used for measurements of SAW phase change (sensor response) as a function of time. The measurement chamber was purged with a carrier gas (nitrogen) at a constant rate. The flowing rate was controlled in the range from 5 cm^3/min to 70 cm^3/min

unit (is not shown in Fig.4). A gas sample with a volume with an error not more than ±1%.by a special electronic of 4 cm^3 was introduced into the carrier gas by a conventional method employed in the gas chromatography (using a six-way chromatographic valve (4) and a calibrated 4 cm^3 dosage U-shape tube (3)).

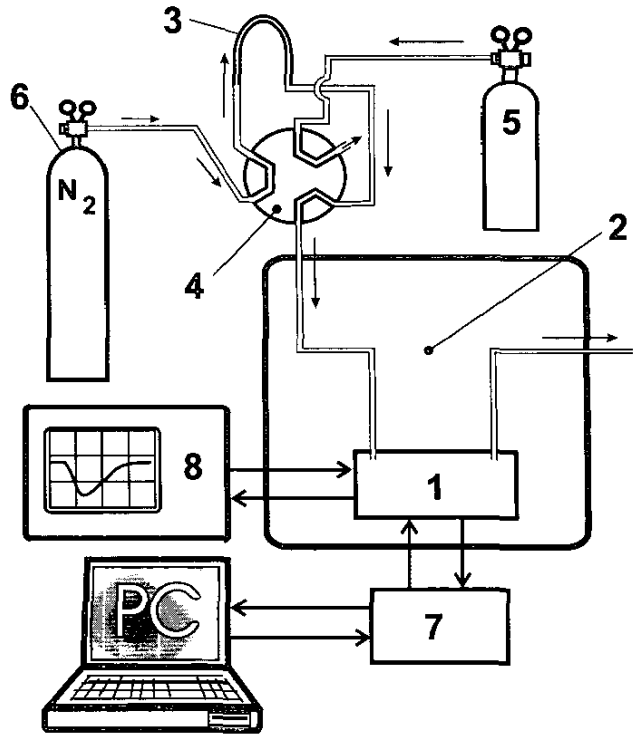

Figure 4. Diagram of measurement system. 1-measurement chamber with SAW sensor; 2-thermostat; 3-U-shape dosage tube; 4-six-way valve; 5-cylinders with propane-butane mixtures; 6-cylinder with nitrogen; 7-temperature control unit; 8-HP network analyzer.

Fig.5 shows the response (the output signal phase change) of a SAW sensor with one and two glass spacers to the injection of a propane-butane mixture at two temperatures of the SAW substrate and at gas flow rate 70 cm^3/min. The output signal phase change was positive (SAW substrate cooling) when the initial SAW substrate temperature was higher than that of the gas sample (i.e., of the chamber walls) and the change was negative (SAW substrate heating) in the opposite case. An analysis showed that the main contribution to the sensor response is probably related to a difference between the heat capacities of nitrogen (1.46 kJ/(kg K) and a propane-butane mixture (1.04 kJ/(kg K), rather than to the difference between thermal conductivities ($2.4 \cdot 10^{-4}$ W/(m·K) for nitrogen versus $1.43 \cdot 10^{-4}$ W/(m·K) for the gas mixture).

The sensor response value, as we could expect, was appeared to be strongly dependnt on the rate of the gas flow and a difference between the temperature of the injected

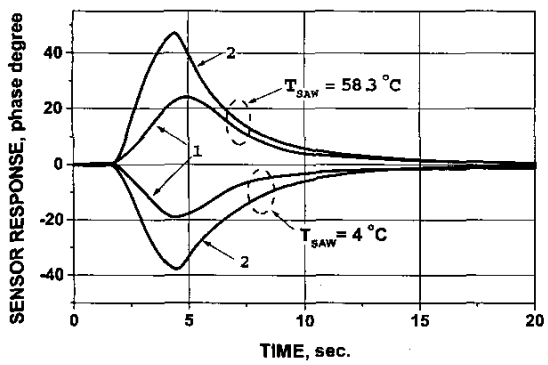

Figure 5. SAW sensor output signal phase changes a function of time in response to injection of a 100% propane-butane mixture. Curves (1) - one and curves (2) - two glass spacers between TEE surface and SAW at a SAW substrate temperature of 58.3 ^{0}C and 4 ^{0}C. The gas temperature was 30 ^{0} C.

gas and that of the TEE working surface. The sensor response value decreased proportionally with the decrease of this temperature difference and changed the sign at this difference sign changing. The measured response dependence on the gas flow rate is given in Fig.6.

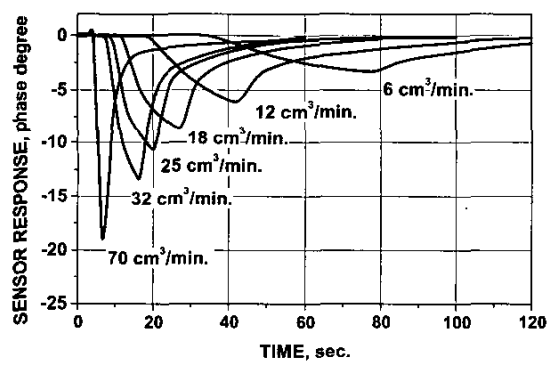

Figure 6. SAW sensor output signal phase changes as a function of time in response to injection of a 100% propane-butane with gas flow rate as a parameter. Single spacer between SAW substrate and TEE. SAW substrate temperature 4 ^{0} C. Gas temperature 30^0 C.

The response of this SAW sensor (with a single glass spacer) to a mixture of 5 vol % of propane-butane and 95 vol % of nitrogen at a flow rate of 70 cm 3 /min, a SAW substrate temperature of 58 ^{0}C, and a gas temperature of 30 ^{0}C was 2.5 phase deg, which falls within a reliably measurable range (in our experiments, a minimum reliably measured phase change was 0.2 phase deg).

When such a SAW sensor with glass spacers was used for detecting the vapors of a series of alcohols and water at a SAW substrate temperature below the gas sample temperature, the response level was approximately the same or slightly higher as that reported previously [7], where an analogous device was employed with a usual temperature stabilization system.

CONCLUSION

Thus, we have described for the first time the basic principles of a SAW gas sensor capable of detecting both the vapors of volatile substances and the stable and burning gases. As preliminary experimental results show the sensor offers high temperature stability and fast response inherent in the SAW sensors of the mass-sensitive type.

Further investigations aimed at the optimization of sensor design parameters and operation regimes would provide, by our opinion, for good prospects in the practical use of such a new SAW gas sensors.

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