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OPTOELECTRONIC SENSORS FOR DETERMINING AMMONIA IN THE ENVIRONMENT

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Abstract. *The creation of an optoelectronic sensor for determining ammonia in the environment using a sensitive element based on phthalic acid salts is considered. The results of studies of such sensors, their stability and sensitivity, as well as the possibility of using them in integrated sensor systems are presented. In the presented sensor, of the light waves passing through the gas, only those that are included in the absorption spectrum of this gas will be absorbed. Thus, by applying (also with the help of a multimode optical fiber) the light coming out of the vessel with the gas to the light detector, it is possible to determine the type of gas and measure its concentration. Similar gas sensors can be used for remote monitoring of the degree of atmospheric pollution (gases N_2 O_2 , NH_3 , CH_4 , etc.) and the concentration of combustible gases (CH_4 , C_3H_8, etc.). For example, a monitoring system for the concentration of CH_4 gas was implemented at a distance of more than 20 km. To eliminate the influence of instability of the radiation source and increase the measurement accuracy, you can use a two-channel scheme, in which the light from the source is split into two beams. One beam, hitting the first photodetector, generates a reference signal, and the second, passing through the sensitive element and hitting the second photodetector, generates a gas-dependent signal. At the output, the signal difference is measured, which is a function of the gas concentration.*

Keywords: *optoelectronic sensor, sensitivity, stability, ammonium, LED, photodiode, phthalic acid salt.*

Introduction.

Among the wide variety of sensors, gas analysis sensors play an important role, which can be explained by the need to reduce energy costs in various technological processes and the need to control the environment and workplaces. Today, there are quite a large number of different methods for gas analysis, but they require both more complex auxiliary equipment and additional energy costs [1-3]. This makes their application in the Internet of Things very difficult. The proposed method is more universal, gives a relatively small error within the measured values, is easy to use and to build sensors based on it.

However, despite extensive research in the field of semiconductor gas sensors, the industrial use of such sensitive elements has some difficulties, among which the problem of creating a stable and sensitive to the analyzed gas sensitive element is one of the most important [4].

The solution to the problem of selectivity is associated with design and analytical solutions based, for example, on the use of selective membranes or sensor systems in conjunction with a method for recognizing a detected molecular product.

At the same time, the main way to improve the efficiency of semiconductor gas sensors is research related to the modification of the structure and composition of active elements [5].

The principle of operation of the gas analyzer.

The main elements of optical sensors are light-emitting (light source) and light-receiving devices, an optical sensitive element. In addition, a connection is required between these elements, which forms a measuring system with a sensor.

Of the light waves passing through the gas, only those that are included in the absorption spectrum of this gas will be absorbed. Thus, by examining the light coming out of a container with a gas using a light detector, it is possible to determine the type of gas and measure its concentration.

Any optical adsorption gas analyzer, the operation of which is based on the absorption of radiation, in its simplest design contains a radiation source 1, an absorption chamber 2 (cuvette) filled with the gas under study and a radiation receiver 3 (Fig. 1).

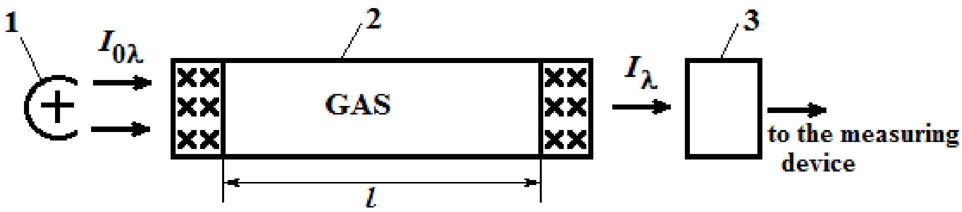

Figure 1 – Scheme of an adsorption optical gas analyzer

The absorption of radiant energy by a gas is determined by the known relation

$$I_{\lambda} = I_{0\lambda} e^{-\alpha c l}, \quad (1)$$

where $I_{0\lambda}, I_{\lambda}$ is the intensity of the monochromatic radiation flux before and after the absorbing gas layer, respectively; α – absorption coefficient is typical for a given gas and wavelength; *c* – is the concentration of gas absorbing radiation; *l* – is the length of the absorbing gas layer.

From this expression it is clear that the metrological characteristics of the gas analyzer depend on the intensity and stability of the radiation source, the spectral characteristics of the emitter and its monochromatism; cuvette length; gas pressure, which affects the number of absorbing molecules per unit volume, that is, the volume concentration of the selectivity of the photodetector.

Semiconductor LEDs and laser diodes, which have a narrower range of the emission spectrum, are used as emitters. Since information is carried only by a part of the transmitted radiation spectrum, which coincides with one of the absorption regions of a given gas, an optical filter can be placed after the emitter that transmits precisely this region of the spectrum. Photodiodes and phototransistors are used as photodetectors.

Gas analyzers based on the absorption (adsorption) of infrared rays are selective and sensitive.

Infrared radiation is absorbed by gases whose molecules consist of two or more different atoms or ions. Gases such as O_2, N_2, H_2, Cl_2 and all inert monatomic gases

(He, Ne, Ar, etc.) are “transparent” in the infrared spectrum. In gases with a complex molecular structure, vibrational-rotational and purely rotational degrees of freedom are observed. As a result, the absorption spectra have a complex structure that is quite individual for each gas, which determines the high selectivity of the method. The absorption of ultraviolet radiation by gases in the region from 200 to 400 nm is accompanied by phenomena that do not occur in the infrared spectrum.

Monatomic gases are characterized by line or resonance spectra associated with the transition of electrons in the atom from the main energy level to higher discrete levels. For example, mercury vapor has clear resonance lines, especially at $\lambda = 253.67$ nm.

The absorption spectra of diatomic and, especially, polyatomic molecules are a set of broad bands, individual lines, as well as areas of continuous absorption.

Therefore, the selectivity of the method for monatomic gases can be quite high, which cannot be said for other gases. Successful implementation of the gas analysis method using ultraviolet absorption is possible only if the measured component has an absorption spectrum that does not coincide with the adsorption spectra of other components of the gas mixture. Not a large number of existing gases have such properties, which limits the scope of application of ultraviolet absorption gas analyzers. These include vapor analyzers for mercury, chlorine, benzene, ozone and other gases. The selectivity and sensitivity of the method can be increased by using monochromatic radiation sources or corresponding broadband emitter monochromators, which is associated with an additional complication of the analyzer design.

Such gas sensors can be used for remote monitoring of the degree of atmospheric pollution (gases N_2O_2, NH_3, CH_4, etc.) and the concentration of flammable gases (CH_4, C_3H_8, etc.). For example, it is possible to implement a system for monitoring the concentration of CH_4 gas at a distance of more than 20 km. To improve measurement accuracy, the two-wavelength method can be used.

The practical application of semiconductor materials as gas sensors requires accurate information about the mechanisms of adsorption-desorption processes occurring in such structures. However, back into the gaseous medium, or occupy one of these centers by forming a surface chemical bond.

Based on experimental studies, optoelectronic gas sensors have been created based on silicon carbide crystals, the surface of which adsorbs ammonia and at the same time the light absorption coefficient in the IR range of the spectrum changes, as well as sensors based on phthalic acid salts, which can be used in new generation devices for gas analysis. The developed methods make it possible to use microelectronic technologies and create integrated intelligent sensor systems.

Structure and characteristics of the sensor.

A silicon carbide crystal was used as a gas-sensitive element (modulator) in an optoelectronic gas sensor, the surface of which adsorbs ammonia and at the same time the light absorption coefficient changes in the IR region of the spectrum. By the magnitude of the photodetector current, one can judge the concentration of the gas being analyzed.

In Fig. 2 shows the design of an optoelectronic sensor for measuring ammonia concentration in the environment.

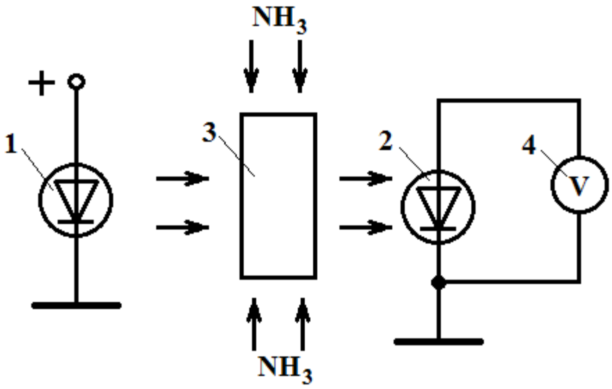

Figure 2 – Optoelectronic sensor design

It contains LED 1, photodetector 2, modulator 3 and indicator 4. It works as follows. When LED 1 is turned on in the forward direction, the light emitted from it with intensity Φ_0 passes through the modulator 3 and hits the photodetector 2 with a lower intensity Φ due to the absorption of light in the modulator. Light Φ incident on the photodetector creates a photoemf at its output (a photodiode was used as a photodetector in photovoltaic mode). If ammonia is introduced into the atmosphere surrounding the sensor, the absorption coefficient of IR radiation by the modulator decreases. This leads to an increase in Φ, and hence in the magnitude of the photoEMF at the output of the photodetector, which is recorded by indicator 4.

As the ammonia concentration increases, the photo emf increases. Such a sensor selectively senses only ammonia and is not sensitive to carbon dioxide, nitrogen, or oxygen. When the volume fraction of ammonia in the external environment surrounding the modulator changes from 0 to 1.5%, the photoEMF value changes from 100 to 150 mV at a constant current through the LED of 90 mA.

If a reagent is placed on the path of propagation of optical radiation that changes its color when interacting with the detected gases or electrolyte, then the optical detector will record a change in the light flux, the real and imaginary parts of which determine the fraction of the light flux reflected from the semiconductor film and the fraction of the flux absorbed in such a film. Accordingly, to find the light absorption coefficient in a semiconductor and the refractive index, measurements are usually taken of the intensity of light transmitted through and reflected from the semiconductor. As a rule, such measurements are carried out in a certain spectral range in order to find certain special points of the spectrum (intrinsic absorption edge, red edge of impurity absorption, etc.).

The reason for the change in the coefficient of absorption (reflection) of light by the reagent when placing an optoelectronic sensor in a gaseous environment is as follows. Short-range forces may exist between the detected gas and the surface of the reagent. The arrangement of atoms on the surface of a solid forms something like a chessboard, defining the concentration of possible adsorption centers. Gas atoms colliding with a surface can either bounce back into the gaseous environment or occupy one of these centers by forming a surface chemical bond.

The process of adsorption leads to a decrease in the free energy of any closed system containing only a free surface and atoms or molecules in a gaseous medium. In this case, a decrease in surface tension occurs, which accompanies adsorption. At sufficiently high temperatures and pressures, the surface tension of some materials can become negative. This means that the surface is unstable and can be rebuilt. In principle, surface reconstruction can also occur at positive values of surface tension. In this case, the coefficient of absorption (reflection) of light from the reagent will vary depending on the concentration of the gas. Surface reconstruction in most cases leads to destruction or a significant decrease in the number of dangling bonds characterized by high energy. Therefore, the most natural interaction between the reagent and the gaseous atmosphere will be the saturation of dangling bonds due to the formation of a local chemical bond on the surface. However, another possibility is also possible due to the weak screening properties of the reagent. It is possible to form an ionic bond, in which charge transfer occurs between the atom (molecule) of the adsorbate and the volume of the reagent, which in turn will also lead to a change in the intensity of light passing through the reagent.

Changes in absorption spectra are described as darkening coefficient spectra (Fig. 3). The darkening coefficient K_d is equal to the ratio of the light transmittance of the film in a clean atmosphere to the transmittance in an atmosphere containing ammonia, i.e. K_d is equal to the multiplicity of the attenuation of the light flux in the presence of ammonia. Within the film thicknesses of 7–12 μm, no definite dependence of K_d on the thickness was found.

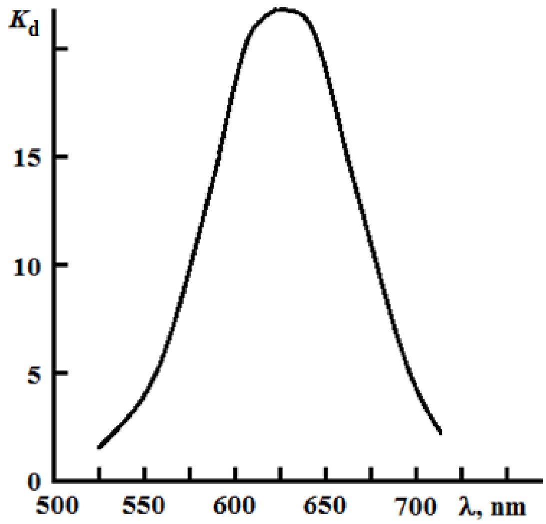

Figure 3 – Spectrum of the darkening coefficient K_d of a gas-sensitive film 10 μm thick in a medium with a volume fraction of ammonia of 30 mg/m^3

Films based on phthalic acid salts can be used as ammonia sensors in an optocoupler pair light emitting diode – photodiode. Therefore, in [6], this property was used in the developed optoelectronic sensor for determining ammonia in the environment.

The structure of such a sensor is shown in fig. 4: an isosceles rectangular prism made of an optically transparent material 1, a layer of phthalic acid salts 2, an LED 3, a photodetector 4, a housing 5 for the photodetector and the LED.

The sensor works as follows. When the LED is turned on, the light emitted from it passes through an optically transparent isosceles rectangular prism 1, is reflected from layer 2 and enters the photodetector with a lower intensity due to partial absorption in layer 2. The light incident on the photodetector creates a photo emf at its output. If ammonia is introduced into the atmosphere surrounding the sensor, then the coefficient of light reflection from layer 2 increases, which will lead to an increase in the photo emf at the output of photodetector 4 (with increasing ammonia concentration). The use of such an optoelectronic sensor with a combined modulator increases the sensitivity to ammonia by more than 10 times. In addition, its performance is also more than 50 times faster than known ammonia sensors. Its adsorption time is about 3...5 s, desorption time is 70...90 s.

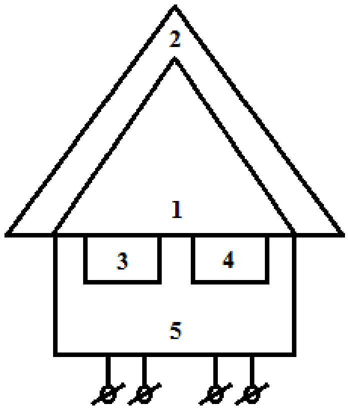

Figure 4 – Structure of an optoelectronic sensor for the determination of ammonia in the environment

Since no current passes through the sensitive element in such optoelectronic sensors, one of the measurement instability factors, electromigration of sensitive material atoms, disappears [6, 7].

To match the absorption spectrum of the gas-sensitive film with the emission of LEDs, the brightest ones were selected, emitting with a maximum at a wavelength of 568 nm with a half-width of ~40 nm.

A silicon photodiode was used as a photodetector. The signal from the photodiode was amplified by an amplifier and sent to the indicator.

When the ammonia concentration in the environment changed from 0 to 30 mg/m^3, the change in the output signal was 0.85 V (Fig. 5). The adsorption time of ammonia by the detector was 13-15 s, the desorption time was 90 s.

The ammonia gas analyzer is designed in the form of a measuring probe connected to the device by a flexible cord. The gas-sensitive film and optocoupler are located in the body of the measuring probe. To protect from external fields and from stray light from the photodiode, a protective metal cover is placed on the probe. The body of the device contains controls and measurement adjustments, an operational amplifier, an indicator and a 9 V power supply.

The degradation characteristics of such a sensor have been studied. In order to be able to judge the change in the characteristics of the gas-sensitive film over time, we studied the aging of the film over the course of one year. For this purpose, ten identical samples of gas-sensitive film were made. The samples were stored in a dry place at room temperature. Film transparency measurements were made using a spectrograph once a month. The film darkening coefficient K_d is the main parameter, the change in time of which must be known, since it determines the stability of the device as a whole. Analysis of the obtained K_d values showed that throughout the entire range of 500-1000 nm, degradation is observed, that is, a decrease in K_d (Fig. 6), which occurs more actively during the first 3000 hours, then it becomes insignificant.

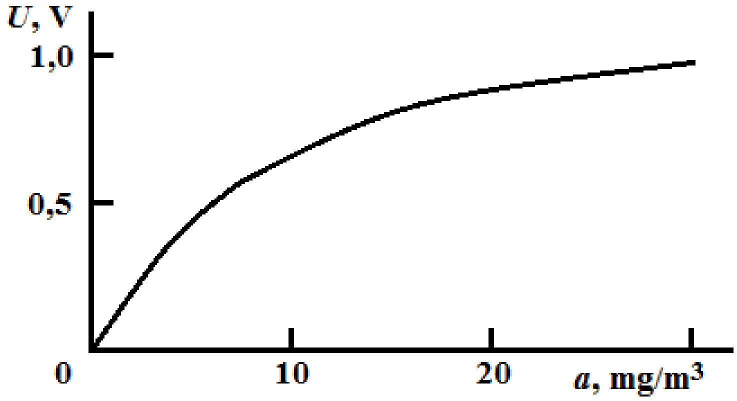

Figure 5 – Dependence of the output signal of the gas analyzer on the volume fraction of ammonia in the environment

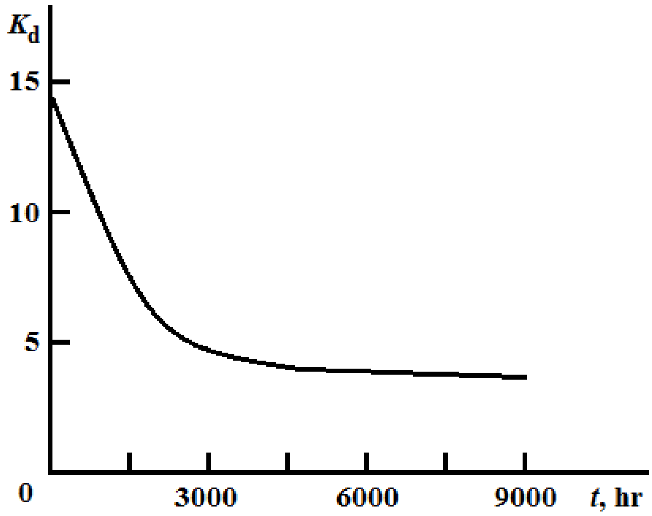

Figure 6 – Degradation of the darkening coefficient K_d

The obtained dependences are typical for all samples of this film. The darkening coefficient K_d varies from 15 for a freshly applied film to 4 after 4000 hours. This means that for practical use it is necessary to subject all samples of gas-sensitive films to artificial aging after application to glass and drying. For this you can use, for example, ultraviolet irradiation.

A freshly applied film has maximum gas sensitivity. After 4000 hours, sensitivity is reduced by 30%, which in turn reduces the efficiency of the device, but can be compensated by increasing the gain in an ammonia-calibrated atmosphere. A stable curve corresponding to 4000 hours of natural aging is a passport characteristic of the device.

To select the optimal mode of the optocoupler, the absorption spectra of gas-sensitive films were measured in the range of 500...1000 nm. In clean air, almost non-selective absorption was observed with an absorption coefficient of 1.1 ... 1.2. As the ammonia concentration in the air increased to 30 mg/m^3, the absorption spectrum of the films changed significantly: it became selective with a maximum at a wavelength of 625 nm and a half-width of 150 nm.

Conslusion.

Among the wide variety of sensors, gas analysis sensors play an important role, which can be explained by the need to reduce energy costs when carrying out various technological processes, as well as the need for remote monitoring of the environment.

However, despite extensive research in the field of creating semiconductor gas sensors, the industrial use of such sensitive elements has some difficulties, among which the problem of creating a stable and sensitive sensor element in relation to the analyzed gas is one of the most important.

The solution to the problem of selectivity is associated with design and analytical solutions, based, for example, on the use of selective membranes or sensor systems in conjunction with a method for recognizing the detected molecular product. At the same time, the main way to increase the efficiency of semiconductor gas sensors is research related to modification of the structure and composition of active elements.

We studied the degradation characteristics of such a sensor. It was found that in the range from –10°C to +35°C the output signal of the ammonia gas sensor does not depend on the temperature both in clean air and in the active medium. The organic origin of the film limits its use to a temperature limit of 45°C, the excess of which can lead to irreversible processes of decomposition of organic components. A change in relative humidity up to 100% has no noticeable effect on the output signal.

On the basis of experimental studies, optoelectronic gas sensors based on phthalic acid salts have been created, which can be used in new generation devices for gas analysis. The developed methods make it possible to use microelectronic technology and make it possible to create integrated and intelligent sensor systems.

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