The optical sensor for detecting NO$_2$ and O$_3$ using a white GaN LED

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Abstract. This article describes the scheme and principle of operation of an optical sensor for detecting nitrogen dioxide (NO$_2$) and ozone (O$_3$) based on the effect of optical absorption spectroscopy. A distinctive design feature of the proposed technical solution is that it is proposed to use an inexpensive powerful white LED based on GaN as an optical radiation source, which has two relatively wide radiation peaks at wavelengths $\lambda$ from 420 to 440 nm and $\lambda$ from 525 to 650 nm. To separate the light streams and form separate measurement channels, three multilayer optical coatings were synthesized: a broadband beam-splitting coating and two narrow-band reflective coatings.

1. Introduction
Nitric oxide is produced from the combustion of coal, oil and gas. If the ignition occurred in a confined space in the presence of oxygen, then when it cools down to the normal temperature, NO is oxidized to NO$_2$, which is already a harmful substance. Nitrogen dioxide is highly toxic. In low concentrations, it irritates the human respiratory tract, and at high concentrations it causes pulmonary edema. Ozone kills microorganisms, so it is used in production facilities for water or air purification (ozonation). Only very small concentrations of ozone are allowed in the air, as it is extremely toxic. Therefore, if the air conditioning systems are broken, the maximum permissible concentrations in the air may be exceeded. Creating an inexpensive sensor using a simple radiation source that can detect the presence of a high degree of concentration of both NO$_2$ and O$_3$ not only improves the safety of life in production, but can also be cost-effective due to its low cost.

A white neutral GaN LED can be used as an inexpensive but powerful enough radiation source for the nitrogen dioxide and ozone sensor. The fact is that in the continuous absorption spectrum of NO$_2$, the region of absorption maxima falls on the wavelength range from 390 to 450 nm, and the region of maxima in the absorption spectrum of O$_3$ is located in the wavelength range from 560 to 620 nm. The regions of maxima in the gas absorption spectrum correspond to the regions of intense radiation at the wavelengths of 437.5 and 600 nm in the spectrum of GaN LED. The LED emission spectrum is shown in figure 1 below.

2. Methods for determining refractive indices
The sensor design is shown in figure 2. The main reference propagation channel in the air is represented in the diagram by black lines. It is placed inside a sealed sensor block and is configured to propagate electromagnetic waves with a wavelength of $\lambda_1$=600 nm. The channel for O$_3$ detection is controlled by
attenuation when radiation with a wavelength of $\lambda_1=600$ nm propagates in the external space. It is drawn with gray lines. To detect NO$_2$, the radiation propagation channel at the wavelength $\lambda_2=440$ nm is used. It is marked with white lines.

![Figure 1. Distribution of radiation power in the spectrum of GaN LED.](image1)

Figure 2. The scheme of the detection sensor for detecting NO$_2$ and O$_3$.

The sensor works as follows. The radiation is generated in a neutral white led and is directed through a focusing optical system to a narrow-band reflecting mirror 1, which serves to reflect energy with a wavelength of $\lambda_2$ and transmit it at a wavelength of $\lambda_1$. It is a multi-layer optical coating installed at an angle of $45^\circ$ to the direction of arrival of the incident radiation.

The flow at the wavelength $\lambda_1$ then falls on a narrow-band reflecting mirror 2 and then goes to the beam-splittting coating 3. Using the beam-splitter, both the internal-air propagation channel, indicated by black lines, and the external channel at the wavelength $\lambda_1$ are formed. Radiation propagating through the internal channel falls on the photodiode and ADC1. This part is used to control the radiated power and operability of the emitting led, as well as to generate a different signal with the participation of a signal that propagated in an external channel with a wavelength of $\lambda_1$. In this case, all amplitude differences caused by the presence of a different configuration of optical elements in the propagation channels are compensated in the signal processing unit. The part of the electromagnetic energy with the
wavelength $\lambda_1$ that allows detecting the presence of O$_3$ by its attenuation is output from the sensor through the interference filter 4 and passes on the propagation path through two narrow-field reflecting mirrors 2 installed at an angle of 45°. After that, it is returned to the sensor through the second interference filter 4, gets to the led and is digitized using the ADC2.

The other part of the radiation that is reflected from mirror 1 at the wavelength $\lambda_2$ is used to detect NO$_2$. It is output through an interference filter 5, propagates between two narrow-band reflective coatings 1 installed at an angle of 45°, and through a second interference filter 5 enters the photodiode and ADC3.

The signal processing unit is formed by differential signals coming through different propagation channels. In this case, attenuation is detected outside the sensor at the wavelengths of 440 nm and 600 nm, which allows the presence of NO$_2$ or O$_3$ with a dangerous concentration to be detected.

The selection of wavelengths for detecting O$_3$ and NO$_2$ takes into account their absorption spectra, shown in figures 3 and 4, respectively [1,2].

![Figure 3. Dependence of the absorption cross section of O$_3$ on the wavelength.](image1)

![Figure 4. Dependence of the absorption cross section of NO$_2$ on the wavelength.](image2)

In the NO$_2$ absorption spectrum at a wavelength of 440 nm, one of the local maxima is observed, in which the absorption cross-section is $7.5 \cdot 10^{-19}$ cm$^2$/molecule (independent of temperature), and the
absorption cross-section at a wavelength of 600 nm is $9.5 \cdot 10^{-20}$ cm$^2$/1 molecule. Thus, if nitrogen dioxide is present in the external channels at the wavelengths of 600 nm and 440 nm, there is a difference between the attenuations on the signal propagation path.

We estimate the amplitude differences arising from optical elements whose composition is different for all propagation channels. As will be shown below, they are used to coordinate the frequency band of the radiated signal with the corresponding attenuation band in each of the external channels.

As follows from figure 3, in the ozone absorption spectrum at a wavelength of 440 nm, the absorption cross-section is $10^{-22}$ cm$^2$/1molecule (and does not depend on temperature), and the maximum absorption cross-section is observed at a wavelength of 600 nm and is equal to $10^{-20}$ cm$^2$/1molecule. Thus, in channels with wavelengths of 600 nm and 440 nm, there is a difference between the attenuations on the signal propagation path under O$_3$ conditions. It allows you to create a corresponding difference signal that compensates for the amplitude differences caused by the presence of a different configuration of optical elements in the propagation channel.

Consider the change in the radiation intensity at $\lambda = \lambda_1 = 600$ nm in the air (reference) channel of length $l_0$ inside the sensor. On the propagation path, this radiation passes once a reflecting narrow-band mirror with a transmission coefficient $T_1(\lambda_1)$ and one reflecting coating with a reflection coefficient $R_1(\lambda_1)$, then falls on a beam-splitting coating with a reflection coefficient $R_0(\lambda_1)$. Thus, the change in intensity will amount

$$J(\lambda)/J_0(\lambda_1) = T_1(\lambda_1)R_2(\lambda_1)R_3(\lambda_1)\exp(-\alpha(\lambda_1)l_1) = A_1 \exp(-\alpha(\lambda_1)l_1),$$

where $\alpha(\lambda_1)$ is the specific attenuation in air, equal to $3 \cdot 10^8$ cm$^{-1}$, $A_1$ is the coefficient that takes into account the decrease in the amplitude in the optical elements on the propagation path.

We analyze how the radiation intensity $J_0(\lambda = \lambda_1 = 600$ nm) changes in channel with length $l_1$ in the presence of a dangerous O$_3$ density of $\beta_1 = 2 \cdot 10^{-3}$ g.m$^{-3}$. At the specified concentration, the number of O$_3$ molecules in 1 cm$^3$ will be

$$B_1 = \beta_1 \frac{N_a}{10^6 M(O_3)} = 2.5 \cdot 10^{13} \text{ cm}^{-3},$$

where $N_a = 6.02 \cdot 10^{23}$ mol$^{-1}$, $M(O_3) = 47.99$ g.mol$^{-1}$. We take the value of the absorption cross section $\sigma$ for O$_3$ for $\lambda_1$ and calculate the decrease in the intensity of $\alpha$ O$_3$ with propagation by 1 cm:

$$\sigma(\lambda_1) = 10^{-20} \text{ cm}^2; \alpha_{O_3} = B_1 \sigma(\lambda_1) = 2.5 \cdot 10^{-7} \text{ cm}^{-1}.$$

The radiation intensity that reaches the photodiode with ADC2, taking into account the optical elements on the propagation path, refers to the initial intensity as follows

$$J_2(\lambda)/J_0(\lambda_1) = T_1(\lambda_1)T_3(\lambda_1)[R_2(\lambda_1)]^3[T_5(\lambda_1)]^2\exp(-\alpha_{O_3}(\lambda_1)l_1) = A_2 \exp(-\alpha_{O_3}(\lambda_1)l_1).$$

On a photodiode with ADC3, in turn, the change in intensity associated with attenuation and occurring in the presence of a dangerous NO$_2$ concentration is determined by the ratio

$$J_3(\lambda)/J_0(\lambda_2) = [R_1(\lambda_2)]^3[T_4(\lambda_2)]^2\exp(-\alpha_{NO_2}(\lambda_2)l_2) = A_3 \exp(-\alpha_{NO_2}(\lambda_2)l_2).$$

Note that the dangerous concentration of NO$_2$ is $\beta_2 = 2 \cdot 10^{-3}$ g.m$^{-3}$ and $M(NO_2) = 46$ g.mol$^{-1}$. Given this data, we calculate

$$B_2 = \beta_2 \frac{N_a}{10^6 M(NO_2)} = 2.6 \cdot 10^{13} \text{ cm}^{-3}, \sigma(\lambda_2) = 7.5 \cdot 10^{-19} \text{ cm}^2; \alpha_{NO_2} = B_2 \sigma(\lambda_2) = 2 \cdot 10^{-5} \text{ cm}^{-1}.$$
The calculation results show that there are significant differences between $\alpha_{\text{NO}_2}$, $\alpha_{\text{O}_3}$, and $\alpha$ in air. As the practice of using separate gas sensors for detecting ozone and nitrogen dioxide shows, when the signal accumulates for a time interval of 20–30 seconds and at $l_2$ and $l_1$ of the order of 50 cm, the presence of a dangerous concentration of NO$_2$ or O$_3$ can be detected. When generating difference signals, the corresponding amplitude correction occurs, taking into account the $A_i$ coefficients.

3. Reflecting, beam-splitting and transmitting optical elements of the sensor

To improve the accuracy of gas concentration measurements, it is necessary to strive for the best match between the spectrum band of the propagating signal and the area of maximum attenuation in gases. As shown at figure 2 scheme this is not only due to the choice of an appropriate radiation source [3,4]. Given that the led has two radiation maxima, the required frequency selection is achieved by synthesizing optical elements with certain frequency characteristics by forming thin multi-layer film coatings.

The exception is interference filters 4 and 5 for output and reception of radiation with wavelengths $\lambda_1$ and $\lambda_2$. To implement the sensor, low-cost filters manufactured by Salvo Technologies were selected: CO674-71 with a wavelength of 600 nm and a bandwidth of 13 nm [5] and CO674-72 with a wavelength of 440 nm and a bandwidth of 20 nm [6], whose transmission spectra are shown in figures 5 a and 5 b, respectively.

The mirrors 1 and 2, as well as the beam-splitting coating 3, which were located at an angle of 45° relative to the direction of arrival of incident radiation, were synthesized separately using the "FilmManager" program [7-14].

Figure 6 shows the reflection spectrum of mirror 2 for $\lambda_1=600$ nm, which is formed on a glass substrate coated with 12 alternating layers of ZrO$_2$ and MgF$_2$ with layer thicknesses: 159.6 nm; 152.1 nm; 148.4 nm; 143.1 nm; 150.5 nm; 163.8 nm; 151.7 nm; 144.7 nm; 148.6 nm; 140.5 nm; 181.7 nm and 200.4 nm.

Figure 7 shows the reflection spectrum of mirror 1 for $\lambda_2=440$ nm, which is made on a glass substrate coated with 14 alternating layers of ZrO$_2$ and quartz with the layer thicknesses: 95.4 nm; 91 nm; 103.3 nm; 92.9 nm; 99.8 nm; 93.8 nm; 91.8 nm; 98.3 nm; 94.6 nm; 97.9 nm; 97.8 nm; 91 nm; 126.2 nm and 139.2 nm.

**Figure 5.** The transmission spectra of filter CO674-71 for $\lambda_1$ (a) and filter CO674-72 for $\lambda_2$ (b).
Figure 6. Spectrum of the synthesized mirror 2 for $\lambda_1=600$ nm.

Figure 7. Spectrum of the synthesized mirror 1 for $\lambda_2=440$. 
Figure 8. Spectrum of the synthesized beam-splitting coating 3 for $\lambda_1=600$ nm.

Figure 8 shows the reflection spectrum of the beam-splitting coating for $\lambda_1=600$ nm, which is formed on a glass substrate coated with 6 alternating layers of ZrO$_2$ and quartz with the layer thicknesses: 98.4 nm; 134.4 nm; 148.6 nm; 148.1 nm; 137.4 nm and 80.3 nm.

4. Conclusion

Thus, in this paper, an optical sensor scheme was proposed for detecting the presence of dangerous concentrations of NO$_2$ and O$_3$ gases using a low-power white GaN LED as a radiation source. The proposed sensor design makes it possible to form narrow-band emission lines at wavelengths corresponding to the absorption maxima in the radiation spectrum of these gases dangerous to human health. To implement the optical sensor circuit was synthesized with three layered optical coating: a broadband beam-splitting and two reflective that are allowed to form:

- internal air channel of distribution using mirror 1 reflecting at $\lambda_2=440$ nm and transmits at $\lambda_1=600$ nm, a reflecting mirror 2 and a beam-splitting coating 3 at $\lambda_1=600$ nm;
- external propagation channel using three mirrors 1 reflecting on and two narrow-band filters 5 at $\lambda_2=440$ nm to detect the presence of NO$_2$;
- an external propagation channel using three mirrors 2, a beam-splitting coating 3, and two narrow-band filters 4 at $\lambda_1=600$ nm to detect the presence of O$_3$.

The work was supported by the Russian Science Foundation (RSF, Grant № 19-79-10110).

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