Light emitting diode absorption spectroscopy for combustible gas monitoring

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Abstract. A new generation of the infrared light-emitting diodes (LEDs) and photodiodes (PDs) was used to construct an open path non-dispersive infrared (NDIR) methane analyzer. It was shown earlier that its characteristics are suitable for usual alarm systems, but new measurements have shown that cross sensitivity to other alkanes is rather high.

1. Introduction

Infrared light absorption spectroscopy is widely used for about eighty years [1]. The whole infrared region is usually divided into three regions described in Table 1.

Table 1. Infrared usual regions

| Region | Wavelength | Vibrations          |
|--------|------------|---------------------|
| Far IR | 1 mm - 25 µm | Lattice vibrations, rotations |
| Mid IR (MIR) | 25 - 2.5 µm | Fundamentals       |
| Near IR (NIR) | 2500 - 800 nm | Overtones          |

Recently a new generation of semiconductor heterostructure LEDs was developed for MIR and NIR regions [2].

Practically simultaneously with the development of NIR and MIR LEDs the works on their application for gas detection had started [3-8]. IR LEDs are basically double heterostructures grown on a semiconductor substrate by means of liquid phase epitaxy, the narrow-gap band active layer being located between two wide-gap band layers. For NIR region quaternary heterostructures GaInAsSb/AlGaAsSb lattice matched to GaSb substrate are used, the minimal band gap existing in GaSb - 0.726 eV. For MIR region quaternary heterostructures InAsSb/InAsSbP lattice matched to the InAs substrate are used, the minimal band gap existing in InAs - 0.354 eV. Due to the fact that in narrow-gap band semiconductor the non-radiative relaxation processes dominate radiative ones with temperature growth, the MIR LED optical power saturation happens rather quickly. As a result, the optical power of NIR LEDs is by several orders higher than of MIR ones. For NIR LEDs the typical optical power is tens mW, while for MIR ones – tens µW, these numbers being confirmed by LEDs specifications from “Led Microsensor NT”[9].
Fundamental vibrations of main combustive gas molecules are located in MIR region, while in NIR region mainly overtones are located, the absorption intensity being by several orders lower than for fundamental vibrations [10]. So for LEDs the perspectives of using them for NIR region are practically the same as for MIR one, the absorbance measured values being of the same order.

LEDs could be used only in nondispersive infrared (NDIR) absorption spectroscopy due to the fact that their spectral widths are of the same order as the specific absorption bandwidths. The main peculiarity of NDIR scheme is the use of two channels – of the reference channel (for which LED spectra do not intersect absorption bands) and of measurement one (for which LED spectra cover absorption bands). To exclude the effects of additional scattering and absorption, the measurement channel intensity is normalized to reference channel intensity.

Up to now only MIR LEDs [4-7] or halogen lamps with filters [11] were used for combustible gas detection. The reason for it is the fact that the most strong absorption bands are located in MIR region. Despite it, first, trial attempts of using NIR LEDs for methane detection were started at the end of the previous century [3]. Only after NIR LEDs became a commercial product in the second decade of our century, the new research had started [9,12,13]. The obvious advantage of using LEDs is their small dimensions, low energy consumption, and a rather low price. These LEDs could be used firstly in the cases when measurements of rather high concentrations with a rather low accuracy are needed – in such systems as open path gas analyzers, for which the alarm signal is defined on the level of 10% of the low explosion level, its typical values being of the order of several percents for main combustible gases.

2. Experimental
A prototype of an open path LED-based methane analyzer was constructed recently [12]. It consists of two independent units – emitting and detecting blocks mounted on tripods. In emitting block LEDs from “LED Microsensor NT” company are used (at 2.3 μm wavelength for the measurement channel and 1.7 μm for the reference one). LED spectra and methane and water vapor absorption bands are presented in Figure 1. These LEDs are characterized by the compact size of 0.35×0.35 mm, low power consumption (<1 mW), short response time ~ 10-50 ns, operation temperatures up to +150 °C, lifetime 80 000 hours. LEDs are mounted into a package with a thermoelectric module (Peltier element) enabling LED chip temperature stabilization.

- LED17
- LED23

Figure 1. LED spectra and methane and water vapour absorption bands.
In detection bloc “LED Microsensor NT” NIR photodiode is used with following characteristic: cut off at wavelength 2.45 μm, sensitive area diameter 0.3 mm, detectivity 2·10^{10} cm·Hz^{0.5}W^{-1}. The whole view of the prototype of an open path methane analyzer with the gas cell is given in Figure 2. It was shown in [12], that it could be used for alarm systems.

![Figure 2. The prototype of an open path LED-based methane analyzer](image)

Besides methane, the developed open path gas analyzer is sensitive to all gases with similar absorption spectra, firstly to the gases from the same homological set, alkanes. Weak dependence on gas content is illustrated in Figure 3, in which the transmittance measurements for both reference and measurement channels are presented for two different alkane mixtures - for 85% isobutane + 10% butane + 5% propane mixture and 70% propane + 30% butane one. The transmittance gets lower after the gas cell is filled with gas. It is seen that after equilibrium is achieved the ratio of the intensities of the measurement and reference channels is quite the same, while the gas content is quite different. For improving the selectivity of the gas analyzer to different gases, one can use LED arrays with a set of LEDs emitting light at wavelengths which are near to specific gas absorption bands. Such LED arrays are also available on the market now [9]. The potentialities of using LED arrays for hydrocarbon detection are discussed in [14].

![Figure 3. Transmittance for two different gas mixtures for measurement (2.3 μm) and reference (1.7 μm) channels: a - 85% isobutane + 10% butane + 5% propane; b - 70% propane + 30% butane.](image)
3. Conclusions
It is shown that the NIR LED – NIR PD photocouplers permit one to perform NDIR measurements of combustible gases concentrations within the limits needed for standard alarm systems, but with a rather low selectivity to different alkanes.

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