

Nanostructured light guide sensors of the solvents' vapors in atmosphere

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Abstract: Chemical sensors of solvents' vapors based on different light guides (integrated- and fiber-optics) were designed and tested. The vapor sensitive substances were introduced into nano-scale porous outer layers of the light guide substrate/core. A substrate/core material used was phase separated silicate glass or polyester polymer.

Keywords: Optical Chemical Sensors, Solvent Vapors Detection, Integrated-Optics Components, Fiber-Optics Components, Nano-porous Glass Composition Materials

1. Introduction

Optical sensors of the gas/atmosphere components have demonstrated its good performances and are widely used in analytical practice[1-3]. Of special interest are the light guide (incl. fiber-optic) sensor configurations. The light guide approach to the chemical sensor designing has been offered several years ago[4-8]. In general, an operation principle of those sensors was based on doping the polymer or glass substrate material with species being sensitive to the gas or liquid components of ambient medium. Very advantageous seemed to be saturation of the light guide surface layers with appropriate indicator species. When this layer being enough thin, the sensor response was expected to be theoretically faster. The main problem here consisted in the sensitivity optimization. One of the last successful attempts has been reported in[8] where a plastic optical fiber was coated with a swelling polymer layer containing an active agent. This fiber sensor has demonstrated an acceptable sensitivity to gaseous propane and methane but it was strongly influenced by ambient humidity. So, the known problem of the signal interference remained a matter of urgent interest. Nevertheless this concept seemed to be most prospective one. However, the achieved sensitivity and other detection parameters turned out to be rather insufficient, mainly due to diffusion impediment to the vapor molecules penetration into material[5,7,8]. New ample opportunities have been opened by using finely dispersed materials, particularly, optical micro- and nano-

compositions due to its high specific area contacting with ambient medium[9-12].

Theoretically, there are two approaches to the light propagation through the wave guide being supplied with cladding, they are based on both geometrical and wave optics[13]. In framework of the first one the light being transferred along the waveguide is subject to a phase shift according to the known Goos-Henchen effect. The light is apparently penetrating into cladding material where it may be selectively absorbed by an active agent. In the wave mode approach, this effect is due to penetration of the propagated mode intensity tails into peripheral cladding of the fiber guide.

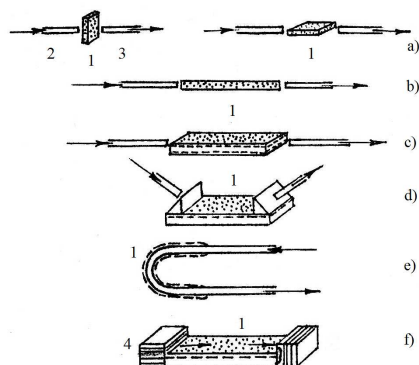
Thus, an appropriate modification of the surface layers composition might influence on the total light attenuation losses in those fiber guides. If the deposited layers carry the gas sensitive agents, then the light transmittance of the samples may be sensitive to the ambient atmosphere gas contents.

In present development, the most appropriate material for substrate (in case of integrated-optics sensors) or for fiber core turned out to be binary-phase separated silicate glass and polyester, respectively. Compositions on the basis of Co^{2+} and Cu^{2+} ions have been chosen as the deposited gas sensitive agents. Our previous investigations have demonstrated its sensitivity to the solvents vapors concentration in atmosphere[14-16]. Those complexes demonstrated more or less expressed absorption/

/transmission spectral bands (in visible and i.r.), strongly influenced by the ambient medium components.

2. Experimental

In principle, only few main designs of the light guide sensors are feasible (Fig. 1).



1 – gas sensitive element; 2 – input fiber; 3 – output fiber; 4 – light source; 5 – radiation detector.

Figure 1. Possible lay-out diagrams of the light guide sensors.

Among them the samples of two kinds have been fabricated and tested in present work (Figs. 1a, 1c and 1e). The first one was flat plates made of the liquated sodium-borate-silicate glass being partially leached-out, so that a porous layer was formed on the sample surface to a certain depth. The gas sensitive species were introduced into nanopores of the layer. The design and technology of those have been presented and discussed below.

The second ones were multimode polymer fibers coated with vapor sensitive compositions. An initial idea was to use the transition metal ion complexes dissolved in the solvents to be detected in atmosphere.

Thus, the sample technologies included the following procedures.

2.1. Sample Preparation

2.1.1. Integrated-optics Samples

At first, the planar wave guides on the said above principle have been developed and tested. Those were thin (0.5 mm) plates carrying a nanoporous layers on its surface.

Original solid glass was liquated sodium-borate-silica glass Na 7/23 with phase separation produced by standard technology[11]. Electron probe microanalysis of the original non-porous glass had shown the Na₂O content being approximately of 6.8 %, boron oxide – 26.7 %, silica – 66.0 %.

Porous samples were produced in course of a stepwise thermal and chemical treatment similar to the well-known Vycor process[9]. After treatment in aqueous solution of 3 N chloric or acetic acid, leaching-out the sodium-borate phase and annealing in air at +550 °C (1 hour), a throughout porous structure permeable to gases and vapours was formed within a silica framework. The Na₂O

content decreased down to 0.2 %, the SiO₂ content was about 87.5 %[12].

An appropriate processing of the measured adsorption isotherms in the capillary condensation area has revealed the prevailing pore size distribution in vicinity of 8 nm, the volume porosity being of 28 %. A calculated specific area was found to be of ~100 m²/cm³.

Depth of the porous layer varied with chemical treatment duration up to 200 μm. Further was a stabilizing annealing procedure at +550 °C (1 hour) in air.

The surface layers were then impregnated with inorganic species being spectrally sensitive to different vapors' molecules. This technology was based on the well developed principle[10,11].

Solubility of the Co(II) and Cu(II) compositions in corresponding solvents was of priority importance. Fortunately, all of them have demonstrated good solubility. Next was a procedure of the porous matrix impregnation in the selected colored solutions until the sorption equilibrium having achieved. The corresponding ions were forced to penetrate into nanoporous glass from the ethanol solutions, so that dissolved ions and complexes remained physically adsorbed on the glass pore surface. That was an Option C in the Table below. The samples were then extracted from the impregnating solutions and dried in air at +50 °C in order to eliminate residual solvent amounts out of the nano-porous matrix. Thereafter an annealing procedure followed at about +150 °C in vacuum (about 10⁻⁴ torr).

2.1.2. Fiber-optics Samples

Several technologies have been tested in order to achieve the desired result. As a fiber material the granular polyester PSM-115 «C» was used. Basically, the fiber was drawn from the polyester preform (Ø20×400 mm) down to 0.5 mm in diameter. In order to prolong the light path in the fiber cladding, the fiber was multiply bended. The loop was dipped into appropriate solution for about 5 min until a surface layer (about 150–200 μm) was softened and partially dissolved and simultaneously modified with selected ions. Then the samples were dried at +50 °C. This sensor prototype is named in the Table below – Option A.

Alternative method was proposed and tested in course of this work. The fiber core material was here a quartz polymer. On its surface a thin layer (100–200 μm) of viscous phenol formaldehyde resin was deposited. Before the resin being solidified, the fiber sample was processed in a finely dispersed (100 mesh) reagent powder (e.g. CoCl₂·6H₂O), so that its particles adhere to the viscous surface. Then the samples were dried at +50 °C (24 hours). This technology had been protected by the Russian Patent[17]. That was – Option B.

2.2. Testing Procedures

The absorption spectra of the samples and of the impregnating solutions were run on the spectrophotometers U-3200 (Hitachi, Japan), Lambda19 (Perkin-Elmer, USA) and SF-26 (LOMO, Russia) in the wave range 300 – 800

nm. The infrared spectra were run with use of the i.r. Fourier-transform spectrometer 5DXC (Nicolett, USA) that enabled the reliable measurements (in wave range $4000 - 400 \text{ cm}^{-1}$) on the samples with optical density up to 4.

In course of experiments the samples were fixed in a holder placed within a blow-through cell being transparent to light. A gas mixture of desired content might be admitted into cell and the spectral absorption might be measured. Before characterization procedure, the samples were kept in the selected gas mixture for sufficiently long time (30 min or longer).

According to the chosen diagrams (Fig.1c and Fig.1e) the measuring lay-outs were arranged. A square-wave carrier frequency of 1000Hz produced by G-28 generator arrived to the input light diode. The signal modulated by sensitive element was received by photodiode, then selectively amplified and recorded.

During testing procedures, the samples were placed within special gas chamber wherein the required atmosphere content was provided.

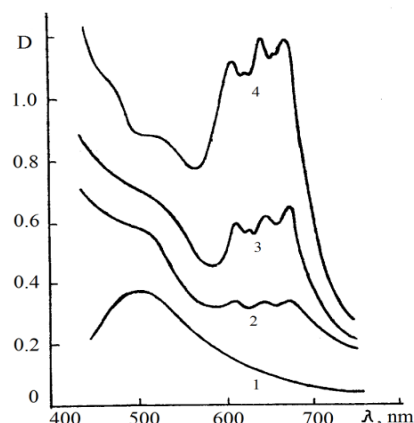
3. Results and Discussion

In Fig.2 the absorption spectra of the porous samples treated in CoCl_2 solutions are presented. The same liquid solution spectrum displays a weak broad band (maximum at 515 nm) caused by electronic quartet transition ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ within octahedral ion $\text{Co}(\text{H}_2\text{O})_6^{2+}$ [18, Ch. 6.2.7]. "Dry" sample spectra present an intensive well structured band within 600–700 nm wave range including feebly marked peaks at 635, 655 and 680 nm. The latter one may be assigned to the ${}^4A_2 \rightarrow {}^4T_1(P)$ transition, other two to the spin-orbital interactions. Mostly notable is dependence of the band height on the ambient air humidity, so that the humidity sensors may be designed on this principle. The plotted graduation curves are given in Fig.3.

In such a way the samples of this kind turned out to be sensitive to the methanol, ethanol and acetone vapors. Provisional parameters of the prototype sensors are presented in the Table below (Option C). Certain mutual signal interference in presence of vapor mixtures took place. However, the response selectivity might be improved by use of a double-wave detection method.

The next active reagent investigated was CuCl_2 . In contrast to the CoCl_2 complexes, the Cu^{2+} ion was able to form only tetrahedral dihydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, so that actually the $[\text{CuCl}_2(\text{H}_2\text{O})_2]$ chains were present [19, Ch. 25.7]. Taking into account an intensive hydrolysis of the CuCl_2 salt in water, methanol as a solvent has been chosen.

In Fig.4 the absorption spectra (in visible and near i.r.) of the pure methanol and CuCl_2 impregnating solution and "dry" samples are presented. Assignment of the spectral bands and lines is scarcely possible because of significant distortion of the copper complexes configuration, nevertheless the absorption bands 700 – 1000 nm, 1000 –



1 – 1M aqueous solution;
2 – nano-porous glass samples in air with relative humidity of 50% (20 °C);
3 – the same in air with relative humidity of 30 % (20 °C);
4 – the same in air with relative humidity of 5 % (20 °C).

Figure 2. Absorption spectra of the CoCl_2 containing samples:

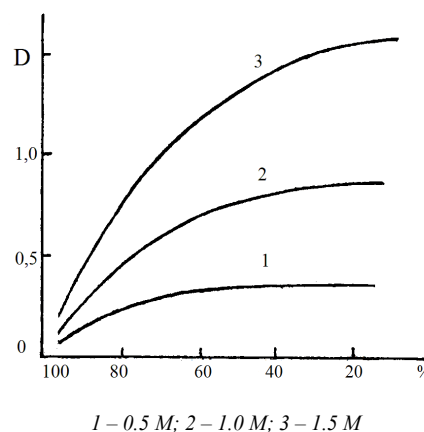


Figure 3. Absorption versus relative air humidity, impregnating CoCl_2 solution concentration being of:

1300 nm and 1850–2000 nm may be caused by tetrahedral $[\text{CuCl}_4]^{2-}$ ions [19, Ch. 25.7]. Noteworthy is a regular transformation of the spectrum shape while variation of the porous layer depth (see Fig.5).

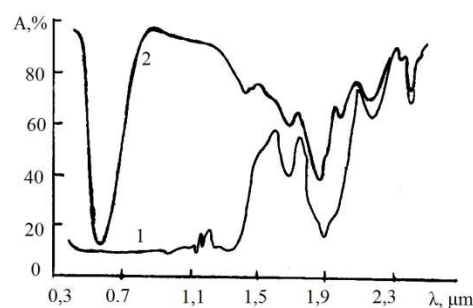


Figure 4. Absorption spectra of the pure liquid methanol (1) and 1M methanol solution of CuCl_2 (2).

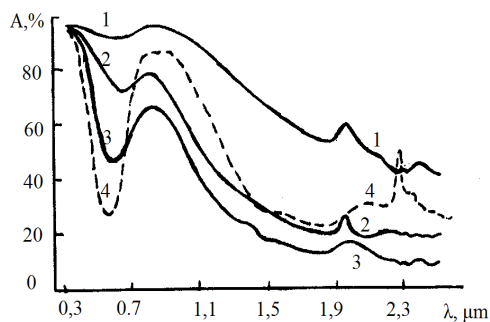


Figure 5. Absorption spectra of the nano-porous samples treated in the CuCl_2 solution, the porous layer being of the depth: 1 – full depth 0.5 mm; 2 – 40 μm ; 3 – 15 μm ; 4 – sample 40 μm in atmosphere with 5 % vol. CH_3OH .

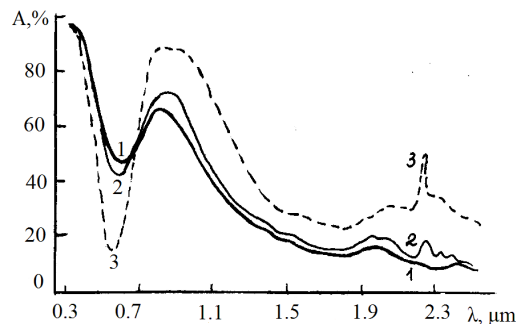


Figure 6. Absorption spectra of the nano-porous samples treated in CuCl_2 solution, being porous to the depth of 15 μm in the atmosphere containing the methanol vapors in concentrations: 1 – 0 % vol.; 2 – 1 % vol.; 3 – 5 % vol.

Spectral response dependence upon the methanol concentration in ambient atmosphere is illustrated in Fig.6. Obviously, this observation opens a way to methanol detection in atmosphere, especially with use of the double-wave method.

In general, the obtained parameters of the prototype sensors of the solvent vapors in atmosphere are compiled in the Table below.

As one can see from the Table, maximum sensitivity to acetone of 0.10 (1/%) was achieved with Option B (quartz fiber+adhesive+ Cu^{2+}), the working wave length being 680 nm. The time constant was about 10 s. Certain signal interference (~15%) was observed in relation to the spirits' vapors. Some less sensitivity to methanol has demonstrated

the prototype (quartz fiber+adhesive+ Cu^{2+}) – Option B, 0.07 (1/%), 580 nm, 10 s. The water vapors influenced on the signal also.

Certainly, the Option A requires further optimization.

Despite the expectations, the planar light guides (Option C) did not exhibit potential advantages, moreover its response time turned out to be too long. The reason may be smooth (not sharp) transition between core and outer areas within the samples due to diffusive mechanism of chemical treatment of glass.

Table. Important parameters of the prototype sensors.

Core material	Characteristic sizes, mm	Indicator composition	Detected vapors' concentration (vol.%)	Sensitivity, 1/% (λ , nm)	Time constant, min
Option A					
Polystyrene	Ø 1	CoCl ₂	CH ₃ COCH ₃ (0.01–5.0)	0.05 (680)	10
		CuCl ₂	CH ₃ OH (0.01–1.0)	0.04 (580)	
Option B					
Quartz	Ø 0.125	CoCl ₂	CH ₃ COCH ₃ (0.01–5.0)	0.10 (680)	0.2
		CuCl ₂	CH ₃ OH (0.01–1.0)	0.07 (580)	0.2
		CoCl ₂	H ₂ O (10-90% rel. humidity)	0.02 (680)	2
Option C					
Glass	0.04–0.5	CoCl ₂	C ₂ H ₅ OH (0.01–5.0)	0.04 (680)	2
		CuCl ₂	CH ₃ OH (0.01–1.0)	0.03 (580)	2
		CoCl ₂	H ₂ O (10–90% rel. humidity)	0.02 (680)	5

Nevertheless the investigations carried out in course of the reported work allow paving the promising ways to developments of optical components being sensitive to the number of important admixtures in ambient atmosphere.

In addition, it should be mentioned that the absorption spectra of solutions were essentially different providing a good opportunity to distinguish simultaneously the signals

from various atmosphere components. Also in this purpose a multiple sensor system and its coordinated signal processing might be mostly helpful.

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