OPTICAL SENSORS BASED ON SINGLE ARM THIN FILM WAVEGUIDE INTERFEROMETER

Performance Report

2-nd Year of Three-year Grant

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1. Objectives established for the second year

The objectives of the project in the initial proposal have been formulated as follows:

1-st Year (1997-1998)

1. Material selection: Materials for the waveguide interferometer will be selected from high temperature polyimide resins doped with thermally stable organic compounds. For specific extra high temperature applications, materials will be selected from the glasses prepared by sol-gel technique and/or possibly from ion-implanted monocrystals.

2. Thin film waveguide fabrication: Fabrication technique will include spin coating, UV curing, and/or ion implantation.

3. Thin film waveguide characterization: This phase of research will include modal spectroscopy based on prism coupling, propagation loss measurement with experimental set up based on imaging with digital CCD camera.

4. Experiments with novel single-arm dual-mode interferometry set up: Optical thin film slab waveguides will be studied with optical set up similar to that described in the proposal (Fig. 1 of the proposal). Testing the interferometer as a temperature and pressure sensor for the gaseous combustion products of aeropropulsion systems will be conducted. The gases to be tested will include CO, CO_2, NO, NO_2, and possibly others.

2-nd Year (1998-1999)

1. Delineation of optical channel waveguides and their characterization.

2. Fabrication of optical coupling elements including gratings and inlets/outlets for optical fibers.

3. Testing the interferometer sensors in optical channel waveguide configuration.

3-Rd Year (1999-2000)

1. Development of purged gas chamber and precise heater for testing single-arm interferometric sensors.

2. Testing the waveguide coupled with optical fiber lines.

3. Estimations of the figures-of-merit of the devices. Conclusions on the feasibility of proposed sensors as elements of aeropropulsion control systems.

2. Actual accomplishments during the second year

The actual accomplishments achieved during the first year are briefly listed below [1]:

1. Material selection: Metal substituted phtahlocyanines were selected and studied as potential indicator dyes that can be used in the waveguide sensor.

2. Design and construction of the experimental purged gas chamber: Experimental set-up includes additional mixing chamber which allows to expose the sensor to a certain gas mixture for a short period of time and therefore to characterize time response. It also includes vacuum sealed multimode fiber line which delivers light to and from the sensor inside the chamber to external signal processing equipment.

3. Preliminary study of the effects of gases adsorbed by polymeric waveguide on its refractive index: The obtained results showed that the refractive index is sensitive to the presence of the gases and that the single-arm dual-mode interferometry can be used in gas sensing. However, quantitative characterization of the interferometric waveguide sensor can be accomplished only after construction of the gas chamber.

The actual accomplishments during the second year are described in details in the following sections.

2.1. Materials selection

The initial plan of work was to build the waveguide interferometric sensor using thin films of high temperature polyimide doped with metal substituted phtahlocyanines as indicator dyes. We have already shown that polyimide Ultradel 9020 from Amoco can be potentially used for planar waveguides delineated by direct writing with medium power UV source [2]. Metal substituted phthalocyanines are thermally stable organic compounds with distinctive optical absorption spectrum giving them deep blue or green

color [3]. We have performed preliminary study of a number of metal substituted phtahlocyanines in order to investigate their potential use as indicator dyes [1]. It was shown that indeed some of them, being dissolved in various solvents, change color in reversible manner in the presence of organic acids. However, understanding of the detailed mechanism of the above mentioned changes requires more significant efforts. In addition, the behavior of the phthalocyanines being embedded within the polyimide matrix is not well predictable yet, because it depends on many factors such as solvent composition, concentration of the polymer in the solvent, concentration of the dye, heat treatment of the film after spin casting, oxidation, effect of atmospheric moisture, etc. The decision has been made to switch to better known indicator dyes embedded into polymer poly(methyl methacrylate) (PMMA). This was done in order to evaluate the performance of the sensor using sensing materials with better predictable features. The used indicator dyes and the experimental data on the change of the optical absorption spectrum and the refractive index of the dye-doped PMMA films after exposure to various gases is presented in Table 1. These data were obtained in the course of the following experiment. An indicator dye was added to the solution of PMMA in chlorbenzene (1 g solids per 10 ml liquids) at a concentration varying from 50 to 10 mM per liter. The solution was filtered with a PTFE filter (0.2-micron pore size). Then it was spin cast on a 1 by 3-inches quartz substrate. The coating was baked in open air at a temperature of 70^0C for one hour. No visible change in the coating was observed after baking. Then the sample was placed into the experimental gas chamber developed during the 1-st year of the project [1]. Within the chamber the sample was mounted between the terminals of the emitting and receiving multimode fibers. The terminals were connected to positive lenses in order to provide collimated beam passing through the sample. The internal fibers were connected by the vacuum feed-through connectors to the external multimode fiber lines. These lines were connected to a Varian Cary 3E UV-Visible spectrophotometer using standard fiber optics coupler. The refractive index of the films was measured using the prism coupling technique. The refractive index of the films was of the order of 1.5 and greater than the index of the quartz substrate (1.457). This provided the condition for using the films as planar light guides. The speed of spin

casting was precisely adjusted to produce a thickness of the films of about 3 micron giving three to four propagating modes at 633-nm wavelength. The extended number of modes gives better accuracy in determining the refractive index. The samples were exposed to the gases listed in Table 1. The gases were deluted in pure nitrogen down to 5% concentration . The pressure of gas mixtures during the exposure was about 600 Torr except NO_2/N_2 mixture which was maintained at a pressure of 100 to 200 Torr.

Table 1. Optical absorption and refractive index change of PMMA thin films doped with various indicator dyes and exposed to various gases (N/C - no change, N/A - not applicable)

N	Indicator dye	Solubility in PMMA/CB	pH(color)	Refractive index of unexposed (633 nm)	Reaction to NH_3		Reaction to CO_2		Reaction to NO		Reaction to NO_2	
					Abs.	$\Delta n \times 10^3$	Abs.	$\Delta n \times 10^3$	Abs.	$\Delta n \times 10^3$	Abs.	$\Delta n \times 10^3$
1	Bromocresole Purple	good	5.2(yellow) ↔ 6.8(blue)	1.5010±0.0010	Peak 400 nm	3.5	N/C	N/C	N/C	N/C	Peak 350 nm	0.1
2	Bromothymol Blue	good	6.0 (yellow) ↔ 7.6 (blue)	1.5014±0.0002	Peak 425 nm	3.4	N/C	N/C	N/C	N/C	Peak 350 nm	0.1
3	Alizarin	medium	5.5 (yellow) ↔ 6.8 red)	1.4997±0.0001	N/C	N/C	N/C	N/C	N/C	N/C	N/C	N/C
4	Neutral Red	poor	6.8 (red) ↔8.0 (amber)	1.4952±0.0001	N/C	N/C	N/C	N/C	N/C	N/C	N/C	N/C
5	Brilliant Yellow	poor with precipitation	6.5 (yellow) ↔ 8.0 (orange)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
6	Nitrazin Yellow	very poor	6.0 (yellow) ↔ 7.0 (blue)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

As one can see from the Table 1, the most significant change of the refractive index was observed for the films made of PMMA doped with indicator dyes Bromocresol Purple and Bromothymol Blue in response to the exposure to ammonia. Some response to NO_2 was also observed. The change of the optical absorption spectra of these films is presented in Fig. 1 through 4. As one can see, both indicator dyes exposed to ammonia demonstrate significant increase of optical absorption in the range 350 to 450 nm. The initially almost colorless films appeared to be yellow after exposure. There is also some noticeable absorption increase near 350 nm in response to NO_2. The color of the films also turned to yellowish. The inrease of the refractive index at 633-nm wavelength is directly connected

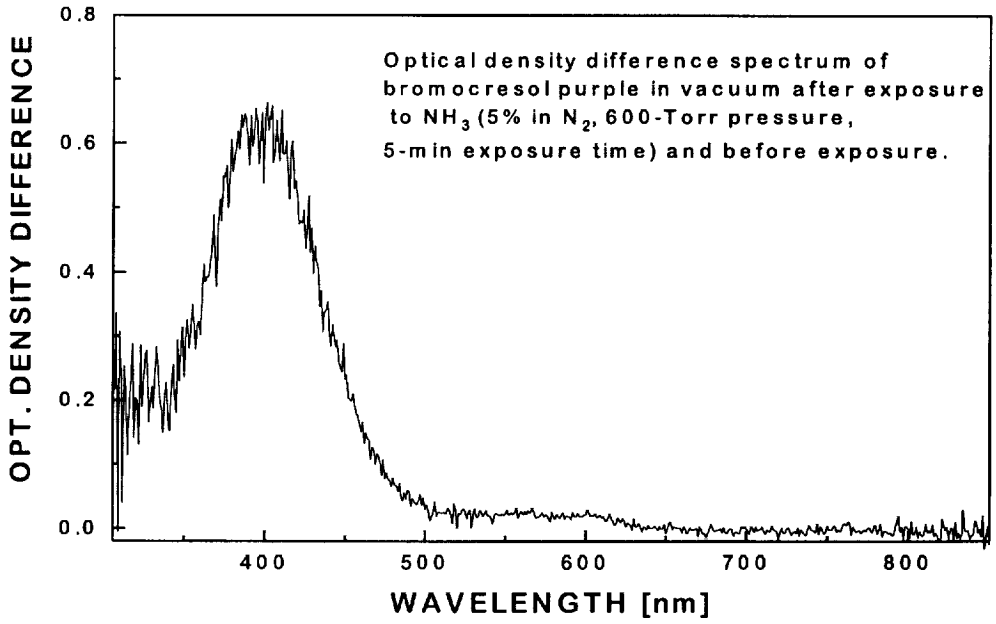
Optical density difference spectrum of
bromocresol purple in vacuum after exposure
to NH3 (5% in N2, 600-Torr pressure,
5-min exposure time) and before exposure.
OPT. DENSITY DIFFERENCE
0.0
0.2
0.4
0.6
0.8
400
500
600
700
800
WAVELENGTH [nm]

Fig. 1

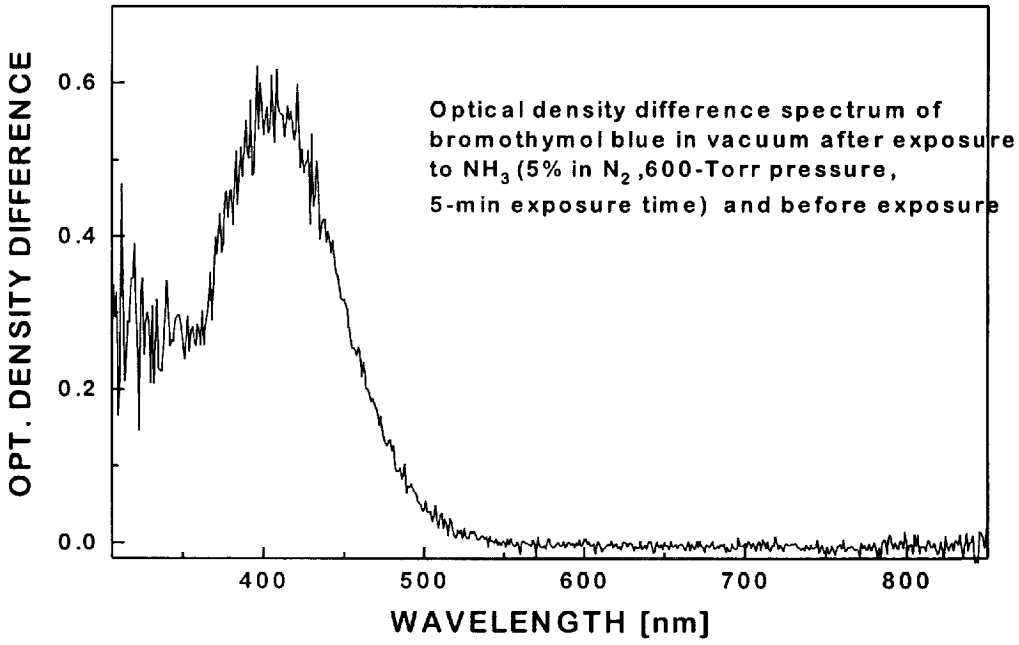
Optical density difference spectrum of
bromothymol blue in vacuum after exposure
to NH3 (5% in N2 ,600-Torr pressure,
5-min exposure time) and before exposure
OPT. DENSITY DIFFERENCE
0.0
0.2
0.4
0.6
400
500
600
700
800
WAVELENGTH [nm]

Fig. 2

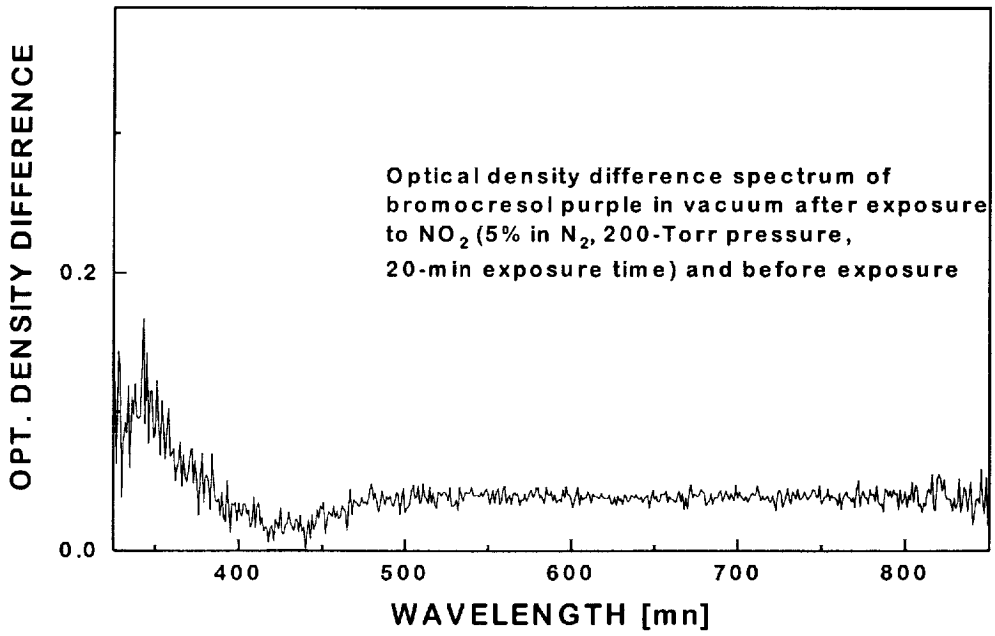
OPT. DENSITY DIFFERENCE
0.2
0.0
400
500
600
700
800
WAVELENGTH [mn]
Optical density difference spectrum of
bromocresol purple in vacuum after exposure
to NO2 (5% in N2, 200-Torr pressure,
20-min exposure time) and before exposure

Fig.3

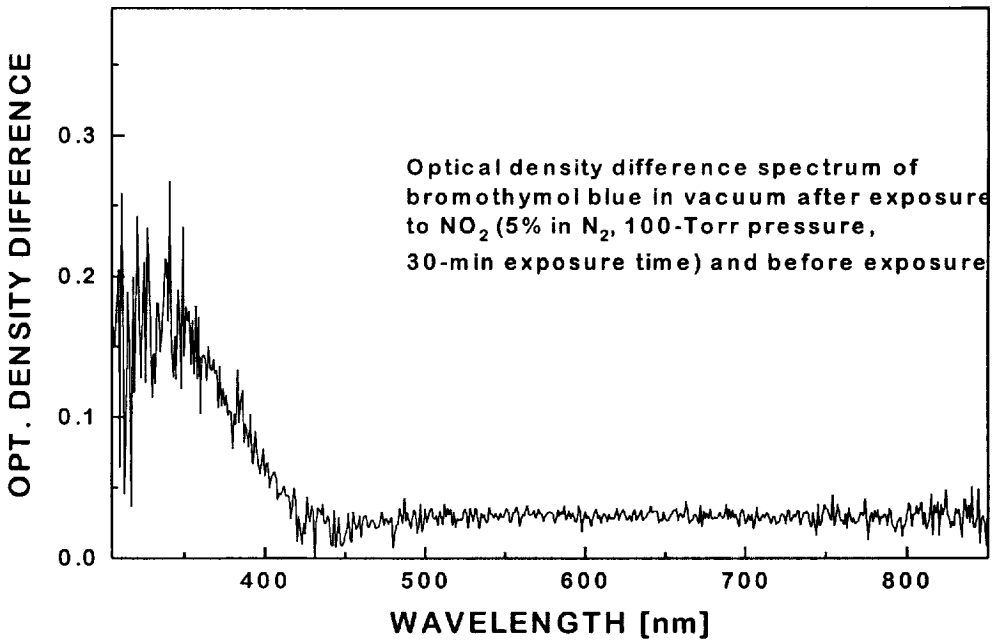
OPT. DENSITY DIFFERENCE
0.3
0.2
0.1
0.0
400
500
600
700
800
WAVELENGTH [nm]
Optical density difference spectrum of
bromothymol blue in vacuum after exposure
to NO2 (5% in N2, 100-Torr pressure,
30-min exposure time) and before exposure

Fig. 4

to the increase of absorption in UV region in terms of Kramers-Kronig relations. It makes these films potentially suitable for the proposed interferometric waveguide sensor. There are however some concerns in regard to these films. Bromocresol Purple, being mixed with buffer solution of NOH in water, exhibits the change of color from purple to yellow when pH changes form 6.8 to 5.2 (neutral to acid) [4]. Klein et al. [5] reported similar behavior (yellow to blue) for the Bromocresol Purple doped into SiO_2 layer prepared by a common sol-gel technique. The film had initially blue color and changed its color to yellow after being exposed to ammonia which acts as an acceptor of proton from the dye and increases pH. In both cases the color change was reversible. Moreover, the color change to yellow corresponded to the increase of the absorption peak near 600 nm. In our case we have irreversible color change and the corresponding spectrum change is different. In addition, we did not observe any noticeable blue or purple shade of the film. Bromothymol Blue in buffer solution of NOH in water changes its color from yellow to blue at a change of pH from 7.6 to 6.0 (slightly acidulous to slightly alkali) [4]. Bromothymol Blue was used in optical ammonia sensor in Ref. 6, 7. The indicator dye was immobilized into a hydrophilic polymer. The change of the color in response to ammonia was reversible. In our case we again had non-reversible change. The other studied dyes have been also used mostly in optical absorption sensors of the gases listed in Table 1 [7, 8]. We however did not observe any noticeable absorption change of the dye-doped polymer films in similar cases. We will therefore continue search for proper dye-polymer mixtures in order to develop compounds with reversible change of absorption and/or refractive index in case of exposure to the gases which are the subject of this project.

2.2. Breadboard prototype of the sensor

Experimental set-up for testing a single-arm dual-mode interferometric waveguide sensor has been already presented in the 1-st Year Report. Fig. 1. shows the schematic of this set-up with the experimental gas chamber. The single-arm dual-mode sensor is

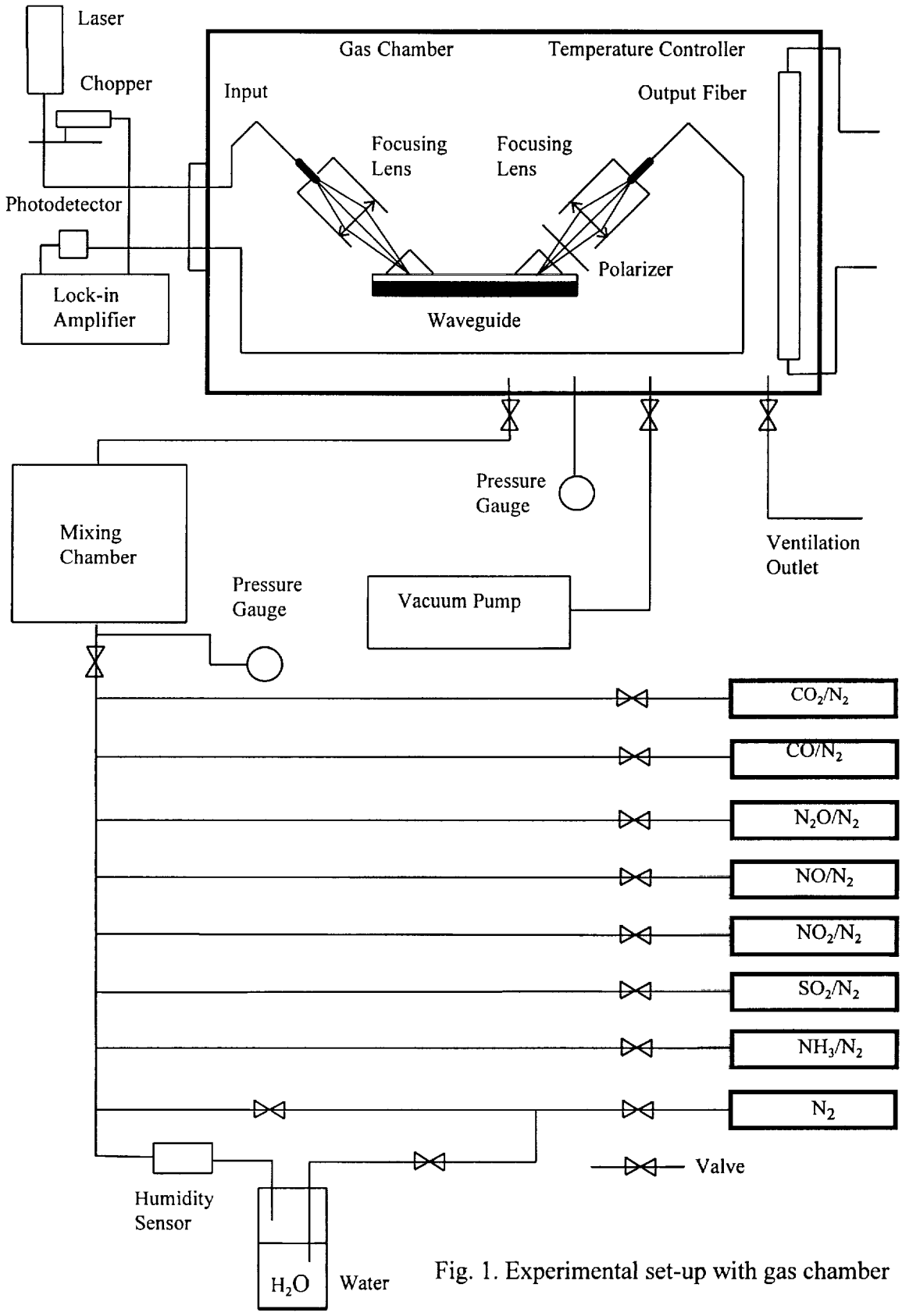

Fig. 1. Experimental set-up with gas chamber

is connected to the light source and the detection and signal processing instruments with multimode optical fiber lines. In order to characterize performance of the sensor in combination with the fiber lines and coupling optics we assembled a breadboard prototype of the optical part of the set-up. The photograph of the prototype is depicted in Fig. 2.

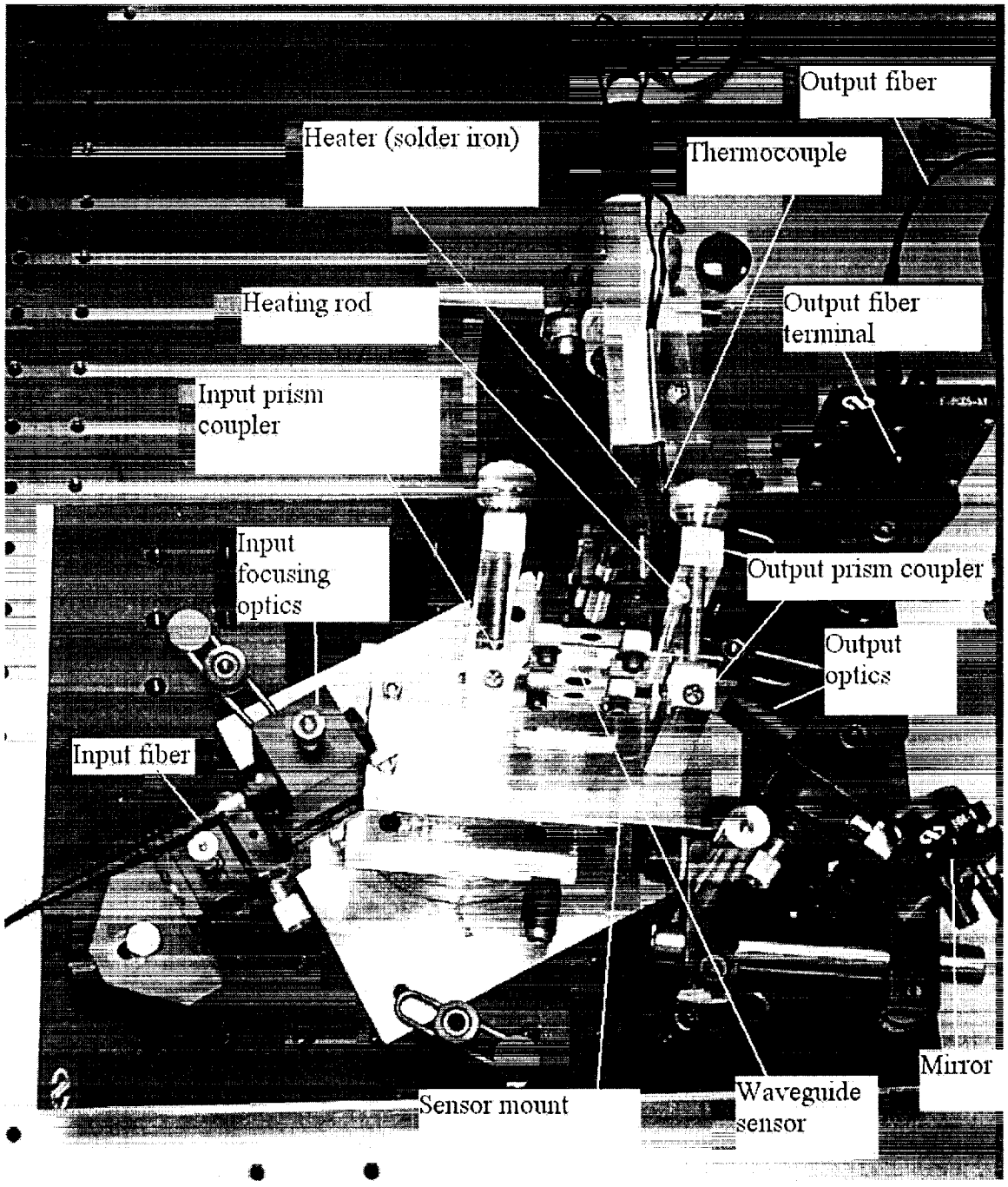

Fig.2. Breadboard mock-up of the sensor coupled to optical fiber lines

The sensor (thin film waveguide made of Bromocresol-doped PMMA in this case) is mounted on a specially designed mount which has two independent prism coupler: input and output. Optical coupling prisms are made of Gallium Gadolinium Garnet(GGG) with a refractive index of 1.9648 at 633 nm. The waveguide is independently fixed to a vertical translation stage by Teflon clips. This design enables selection of any section across the film to be used as a slab waveguide. After vertical positioning the film is pressed against the prisms using rounded knobs with fine threads. The knobs control the degree of optical coupling to the prisms. The waveguide mount is equipped with a rotational table which controls the angle of coupling of the input beam to the waveguide. The light from the input fiber line is focused at the coupling point of the waveguide by a lens. The focusing length of the lens is such that two propagating modes are simultaneously excited (in this case TE_0 and TE_1). The output prism coupler decouples the modes from the waveguide. They propagate after the prism as two separate beams at different angles. The output focusing lens is used to combine these two beams in order them to interfere to each other. A supplemental mirror is used to deflect the beams to the terminal of the receiving optical fiber. The light from the interference pattern is then transmitted through the fiber to a photo detector.

The performance of the sensor was evaluated in terms of its response to the change of the refractive index produced by heating instead of exposure to gaseous agents. The heater was a copper rod bent at right angle and attached to the waveguide from the side of substrate. The rod conducted heat from an electric solder iron. Two thermocouples were attached to the rod. One thermocouple was connected to the chart recorder through an amplifier and continuously monitored the temperature of the rod. The other was connected to an electric thermometer and was used to calibrate the reading of the first thermocouple in degrees of Celsius. Preliminary experiments with the prototype indicated that the input multimode fiber line should be replaced with a single mode fiber. Multimode fiber is a source of intensive speckle noise in the output interference patter which significantly disturbs the output signal upon the change of the refractive index of the film. The speckle noise also slowly fluctuates in time. That makes impossible to filter the signal from these fluctuations using standard modulation/ demodulation technique.

The noise is also very sensitive to the vibrations of the fiber. Replacement with a single mode fiber eliminated all the problems.

2.3. Preliminary results

We performed preliminary experiments with a planar waveguide made of Bromocresol Purple doped PMMA thin film on a quartz substrate. The typical response of the sensor to the variation of the temperature produced by turning the heater on and off is shown in Fig. 3.

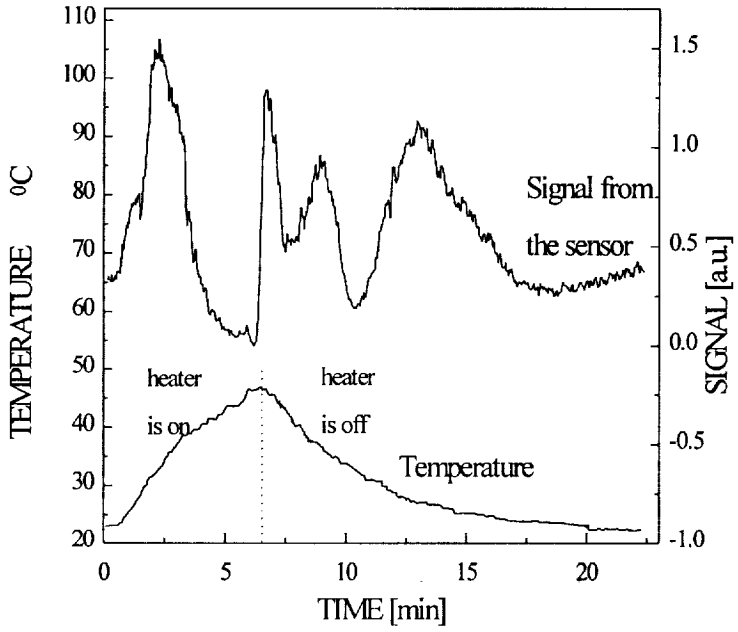

Fig. 3. Response of the sensor during the heating cycle

One can see oscillations of the signal corresponding to the change of the phase difference between the modes of the interferometer. The jump of the signal after turning the heater off is more likely caused by deflection of the substrate. Heating the sensor with a hot rod contacting the substrate does not provide uniform temperature distribution. However at the cooling part of the cycle we assume more uniform distribution of the temperature due to thermoconductive heat transfer over the wide area along the sample. We used the data

for the cooling process to plot the response of the sensor versus temperature. The plot is presented in Fig. 4.

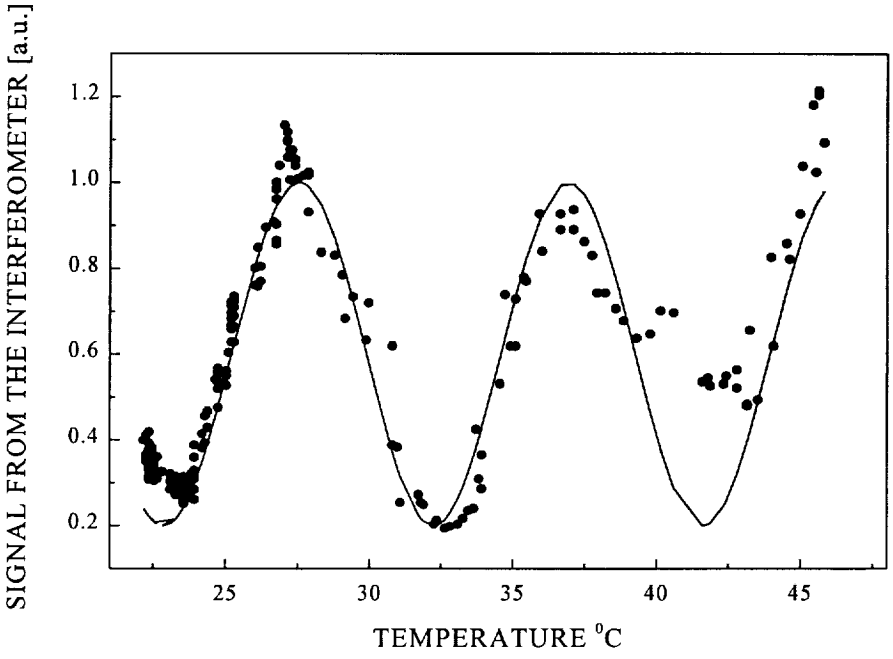

Fig. 4. Signal from the interferometer versus temperature

The sensor signal changes periodically with the temperature change. Approximation of the experimental points with the sine-function gives us a period of oscillations of about 9.37^0C. It allows us to estimate sensitivity of the sensor to the temperature change as 9.37^0C per 2π-phase shift of interfering modes. Assuming that the thermal coefficient of the refractive index ($\partial n / \partial t^0 C$) of the PMMA film is of the order of 10^{-4} $^0C^{-1}$, we have the sensitivity of the sensor in terms of the index of the order of 10^{-3} per 2π-phase shift. Taking into account that we observed a change of the index of 2 to $3x10^{-3}$ in samples exposed to ammonia, we can expect the sensor to be capable of detecting gaseous pollutants.

2.4. List of accomplishments

The following accomplishments have been achieved during the second year:

1. Material selection: The films of PMMA doped with various indicator dyes were studied in the experimental gas chamber. The films doped with Bromocresol Purple and Pmothymol Blue, being exposed to 5% ammonia in pure nitrogen at 600 Torr, exhibited an irreversible increase of optical absorption within a 100-nm band with the center at 400 nm accompanied by an increase of the refractive index at 633 nm of 3.4 to 3.5×10^{-3}.

2. Design and construction of the breadboard prototype of the sensor: The prototype is coupled to a He-Ne laser light source by a single mode optical fiber line and to a receiving detector by a multimode optical fiber line. The coupling is produced with special adjustable prism couplers which can be selectively placed in contact with any point across the sensing film.

3. Preliminary characterization of the breadboard prototype: The prototype showed a sensitivity to the temperature change of 9.37^0C per 2π-phase shift which is equivalent to a sensitivity to the index change of 10^{-3} per 2π-phase shift. This indicates that the sensor is capable of detecting the gaseous agents which are under investigation, particularly, ammonia.

3. Comparison of the accomplishments with the goals and objectives established for the second year

In the course of work it turned out to be more relevant to final goals of the project to substitute the 1-st objective for the second year (delineation of optical channel waveguides and their characterization) with the continuation of the material search for the proposed sensor. The first accomplishment meets this objective. We obtained films based on PMMA doped with Bromocresol Purple and Bromothymiol Blue that are optically sensitive to ammonia and NO_2.

The second achievement meets the second objective for the second year. We chose adjustable prism couplers for connecting the sensor to optical fiber lines in our design of a breadboard prototype of the sensor. These couplers have good coupling efficiency at relatively low cost comparing to any other alternatives such as grating couplers.

The third accomplishment meets the third objective for the second year. We performed testing the breadboard prototype of the sensor using heating as a technique of changing its refractive index. The only difference is that we ruled out the channel waveguides as irrelevant to the final goals of the project. The feasibility of the sensor can be shown for the slab waveguide configuration without usage of relatively expensive technologies of channel waveguide delineation.

4. Objectives for the third (final) year

Since some minor changes in the objectives for the first and the second years took place, the following objectives are proposed for the third (final) year of the project.

1. To finish search for appropriate materials for the sensor. The search will be focused on polymer films doped with indicator dyes.

2. To test the breadboard prototype of the sensor in the test gas chamber. The chamber must be equipped with vacuum feed-through connector for a single mode fiber guiding the light from the remote laser light source to the sensor.

3. To make design of a compact prototype of the sensor.

4. To estimate figures-of-merit of the sensor and make conclusions on its feasibility.

5. To make summary of research.

5. Conclusions

The accomplishments for the second year were focused on the final goal of the project, namely, demonstration of feasibility of a single-arm dual-mode thin film

waveguide interferometer as an environment sensor, particularly, sensor of gaseous agents relevant to aeropropulsion applications. The objectives relevant to the final goal are met by the accomplishments. In the course of the work it was established that the optical fiber line with connects the sensor to the laser light source should be made of a single mode fiber instead of multimode one. Additional efforts were made to do the substitution of fiber lines. Some efforts will be needed during the third year to make a vacuum feed-through connector for the experimental gas chamber.

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Appendix A. List of publications related to the Project

1. Sergey Sarkisov, Andre Taylor, and Putcha Venkateswarlu, Optical sensors based on single arm thin film waveguide interferometers, NASA Lewis Research Center HBCU Research Conference, Cleveland, Ohio, April 9-10, 1997, Abstracts, p. 9.

2. Sergey S. Sarkisov, Michael J. Curley, Darnell Diggs, Huaisong Guo, Ronald D. Clark, and Grigory Adamovsky, "Optical sensor based on single arm dual mode polymeric waveguide interferometer," in *Polymer Photonic Devices*, Bernard Kippelen, Donald D.C. Bradley, Editors, Proceedings of SPIE Vol. 3281, pp. 289-299 (1998).

3. Sergey Sarkisov, Michael Curley, Darnell Diggs, and Grigory Adamovsky, Gas sensors based on single-arm waveguide interferometers, in NASA University Research Centers. Technical Advances in Aeronautics, Space Sciences and Technology, Earth Systems Sciences, Global Hydrology, and Education. Vol. II, Editors: T.L. Coleman, B. White, and S. Goodman, TSI Press, 1998, pp. 257-262.