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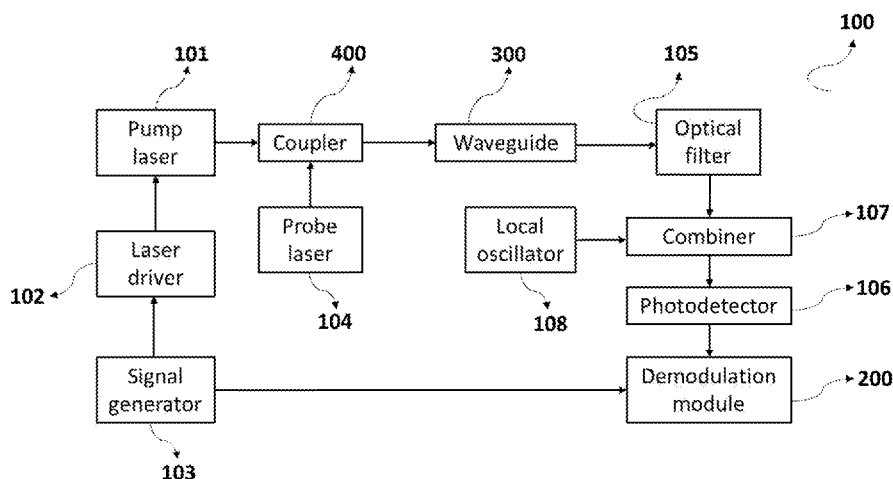
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FIG. 1A



(57) Abstract: A passive-phase-detection photothermal spectroscopy (PTS) system (100) and methods are provided for gas measurements. The PTS system(100) includes a pump laser source (101), a probe laser source (104), the pump and probe laser beams simultaneously propagating through an optical waveguide (300) having a target gas specimen. Moreover, the PTS system(100) can be based on a heterodyne detection scheme and includes a combiner (107) configured to align light input from a local oscillator (108) with the probe laser beam (109) output from the optical waveguide (300) to output to a photodetector (106) that is configured to generate beat notes (111). A demodulation module (200) is configured to detect and measure a photothermal signal based on the beat notes (111) received from the photodetector (106) for gas measurements. The core-cladding-mode interference PTS system (500) can also be based on a core-cladding-mode interference detection scheme and generates the core mode (502) and cladding mode (503) simultaneously for the probe laser source (104) in the waveguide (300).

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PUMP-PROBE PHOTOTHERMAL SPECTROSCOPY HAVING PASSIVE PHASE DETECTION AND AN OPTICAL WAVEGUIDE

CROSS-REFERENCE TO RELATED APPLICATION

5 This application claims the benefit of U.S. Patent Application Serial No. 63/217,096, filed June 30, 2021, which is hereby incorporated by reference in its entirety including any tables, figures, or drawings.

FIELD OF INVENTION

10 This invention relates to gas sensing technology, in particular to gas sensing devices and methods that are based on pump-probe photothermal spectroscopy having passive phase detection and an optical waveguide.

BACKGROUND OF THE INVENTION

15 Photothermal spectroscopy (PTS) is a highly-sensitive, background-free spectroscopic technique for chemical analysis. PTS generally adopts a pump-probe dual-laser configuration, in which a pump laser beam is generated to excite sample molecules and a probe laser beam is generated to simultaneously pass through a heated region with the pump laser beam to induce a phase shift. The concentration of absorptive molecules can then be measured by optical
20 interferometry, since the phase modulation is proportional to the concentration of absorptive molecules.

 For gas analysis, the laser spectroscopy may incorporate optical gas sensors using a gas cell where the laser beams are transmitted through the gas analyte in a single pass or multiple passes to ensure efficient light-gas interactions. Most traditional spectroscopic systems were
25 designed for free-space gas cells including a multi-pass cell such as a Herriot cell or a White cell, or an optical cavity such as a Fabry-Perot cavity with bulky optical elements. Alternatively, the laser spectroscopy may include an optical waveguide in which the light propagation and gas analysis are performed in order to reduce the sensor dimensions and the system complexity, as well as to enhance the light-gas interaction.

30 Compared with the free-space systems, optical waveguides with a small mode field diameter enhance laser intensity and facilitate thermal conduction, improving the sensitivity of

photothermal detection. Several photothermal gas sensor designs based on optical waveguides have previously been investigated, achieving sensitivities higher than the sensitivities of the conventional free space sensors in terms of normalized noise equivalent absorption coefficient. For instance, U.S. Patent No. 9846118B2 discloses designs of a gas sensor in which a hollow core photonic bandgap fiber was filled with target gas and simultaneously coupled with a probe light source and a pump light source. The PTS based on the hollow core fiber achieved a high sensitivity and a large dynamic range for gas detection.

However, the existing PTS systems generally employ a demodulation scheme based on active homodyne detection technique in which the interferometer is required to be stabilized at the quadrature point in order to obtain a linear phase response and a maximum sensitivity, making operations of the interferometer complex and difficult. Moreover, since a servo-control loop is used to monitor the drift of the quadrature point by directly adjusting the probe wavelength or the optical path length via phase modulators, the measurements are sensitive to environmental disturbance. The use of actuators may additionally introduce mechanical and electrical noises to the PTS system. When the environmental disturbance drives the interferometer out of its dynamic range, the servo-control loop has to be reset.

BRIEF SUMMARY OF THE INVENTION

There continues to be a need in the art for improved designs and techniques for a system to measure characteristics of gas specimens with high sensitivities and ease of use without requirement of a servo-control loop system.

Embodiments of the subject invention pertain to a pump-probe photothermal spectroscopic system having passive phase detection and an optical waveguide.

According to an embodiment of the subject invention, a system for gas measurements based on photothermal spectroscopy (PTS) can comprise a pump laser source generating a pump laser beam propagating through a target gas specimen, a wavelength of the pump laser beam being tuned around the absorption characteristics of the target gas specimen to be measured; the pump laser source being simultaneously wavelength and/or amplitude modulated at a frequency, f (in kHz); an optical coupler coupling the pump laser source with an optical waveguide; an optical waveguide configured to transmit the pump laser beams through gas medium containing the target gas specimen to be measured; a laser driver configured to control temperature and

injection current of the pump laser source; a signal generator connected to the laser driver and configured to provide modulation to the pump laser source; a probe laser source generating a probe laser beam connected to the optical coupler and coupled to the optical waveguide; an optical filter connected to an output of the optical waveguide and configured to filter out the pump laser beam and to transmit the probe laser beam. The probe laser beam and the pump laser beam simultaneously propagate through the optical waveguide. The optical waveguide can be an inner-coating hollow core fiber, a hollow-core anti-resonant fiber, or a slot waveguide, disposed in the target gas specimen. Furthermore, the probe laser beam is phase modulated due to the photothermal effect, and the harmonic components of the photothermal phase signal have a linear relationship with a gas concentration of the target gas specimen.

Based on the pump-probe PTS system, embodiments of two systems for the passive phase detection of the probe laser beam propagating through the gas specimen inside the waveguide are provided.

The first photothermal passive phase detection system based on heterodyne interferometry includes, a local oscillator generating a local oscillator light with a frequency shift, Ω (in MHz), with respect to the probe laser frequency; a combiner connected to the local oscillator and an output of the optical filter and configured to align the local oscillator light with the probe laser beam output from the optical filter; a photodetector connected to the combiner and configured to generate beat notes when the probe laser beam and local oscillator light are simultaneously received by the photodetector; and a demodulation module connected to the photodetector and configured to detect and measure a photothermal signal based on the beat notes received from the photodetector for gas measurements. The local oscillator provides a fixed frequency shift (Ω) with respect to the frequency of the probe laser beam.

The demodulation module for extracting the harmonic components of the photothermal phase signal can comprise a splitter, a first mixer, a first reference source, a first low pass filter, a second mixer, a second reference source, a second low pass filter, a divider, a digital arctangent module, a third mixer, a third reference source, and a third low pass filter. The demodulation method can comprise providing, by a reference source, reference signals; generating, by a photodetector, beat note signals; demodulating, by a digital lock-in phase detector, phases of the beat note signals; and demodulating, by a digital lock-in amplitude detector, harmonic signals of PTS from the demodulated phases of the beat note signals for gas measurement. The method

additionally comprises splitting the beat note signals into first and second beat note signals, mixing the first and second beat note signals with an in-phase reference signal and a quadrature reference signal, respectively, and transmitting the first and second beat note signals that are mixed with corresponding reference signals through first and second low pass filters, respectively. The phases of beat note signals are determined by a digital arc tangent method. The demodulated phase signal of the beat note is mixed with a reference at a frequency equal to a multiple of f , such as f , $2f$, or $3f$, and transmitting through a low pass filter.

The second photothermal passive phase detection method based on core-cladding-mode interference can comprise generating, by coupling the probe light into the cladding region and core region of the waveguide, a core mode and a cladding mode simultaneously; generating by a photodetector, the mode interference signals; and demodulating, by a digital lock-in amplifier, the harmonic signals from the mode interference output.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a schematic representation of pump-probe photothermal spectroscopy (PTS) system having a heterodyne interferometry and an optical waveguide according to an embodiment of the subject invention.

FIG. 1B is a schematic representation of the heterodyne beat note signal generation on a photodetector of the PTS system of FIG. 1A, according to an embodiment of the subject invention.

FIG. 2 is a diagram showing harmonic detection of photothermal phase signals from heterodyne interferometry of the demodulation module of FIG. 1A, according to an embodiment of the subject invention.

FIG. 3 is a flow diagram showing a method for gas measurements by demodulating photothermal signals based on the heterodyne PTS, according to an embodiment of the subject invention.

FIG. 4A is a schematic representation of the PTS system having a core-cladding-mode interferometry and an optical waveguide according to an embodiment of the subject invention.

FIG. 4B is a schematic representation of a core mode and a cladding mode propagating along the waveguide according to an embodiment of the subject invention.

FIG. 5A is a schematic representation of the optical waveguide implemented by an inner-coating hollow core fiber according to an embodiment of the subject invention.

FIG. 5B is a schematic representation of the optical waveguide implemented by a hollow-core anti-resonant fiber according to an embodiment of the subject invention.

5 FIG. 5C is a schematic representation of the optical waveguide implemented by a slot waveguide according to an embodiment of the subject invention.

FIG. 6A is a schematic representation of a free-space optical coupler of the PTS system of FIG. 1A and FIG. 1B, according to an embodiment of the subject invention.

10 FIG. 6B is a schematic representation of a fiber-optic coupler of the PTS system of FIG. 1A and FIG. 1B, according to an embodiment of the subject invention.

FIG. 7 is a plot diagram of results of representative photothermal signal profiles measured under different concentrations of N_2O/N_2 gas mixtures by the heterodyne photothermal spectroscopy (PTS) system, according to an embodiment of the subject invention.

15 FIG. 8A is a plot diagram of results of the power fluctuation of the probe laser beam of the heterodyne PTS system, according to an embodiment of the subject invention.

FIG. 8B is a plot diagram of results of continuous monitoring of the first harmonic component of photothermal signals (9 periods) of the heterodyne PTS system under the power fluctuation of the probe laser shown in FIG. 8A, according to an embodiment of the subject invention.

20 FIG. 9 is a plot diagram of results of representative photothermal signal profiles measured under different concentrations of NO/N_2 gas mixtures by the core-cladding-mode interference PTS system, according to an embodiment of the subject invention.

DETAILED DISCLOSURE OF THE INVENTION

25 Embodiments of the subject invention adopt passive phase detection methods including heterodyne detection scheme and core-cladding-mode interference detection scheme to replace the conventional homodyne detection scheme requiring active opto-mechanical stabilization to implement photothermal gas detection.

30 The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items. As used herein, the

singular forms “a,” “an,” and “the” are intended to include the plural forms as well as the singular forms, unless the context clearly indicates otherwise. It will be further understood that the terms “comprises” and/or “comprising,” when used in this specification, specify the presence of stated features, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, steps, operations, elements, components, and/or groups thereof.

Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one having ordinary skill in the art to which this invention pertains. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and the present disclosure and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

When the term “about” is used herein, in conjunction with a numerical value, it is understood that the value can be in a range of 90% of the value to 110% of the value, i.e. the value can be +/- 10% of the stated value. For example, “about 1 kg” means from 0.90 kg to 1.1 kg.

In describing the invention, it will be understood that a number of techniques and steps are disclosed. Each of these has individual benefits and each can also be used in conjunction with one or more, or in some cases all, of the other disclosed techniques. Accordingly, for the sake of clarity, this description will refrain from repeating every possible combination of the individual steps in an unnecessary fashion. Nevertheless, the specification and claims should be read with the understanding that such combinations are entirely within the scope of the invention and the claims.

Referring to FIG. 1A, the heterodyne interferometric photothermal spectroscopy (PTS) system 100 comprises a pump laser source 101 for generating a pump laser beam configured to have the absorption characteristics of a target gas specimen. A wavelength of the pump laser beam can be tuned across the absorption feature of the target gas specimen to be measured. A laser driver 102 is coupled to the pump laser source 101 to control temperatures and injection currents of the pump laser source 101, and a signal generator 103 is also coupled to the laser driver 102 and configured to provide modulations to the pump laser source 101 via the laser driver 102.

In one embodiment, the wavelength and the intensity of the pump laser source **101** can be individually or simultaneously modulated at a frequency of f .

The heterodyne interferometric PTS system **100** further comprises an optical coupler **400** coupled to the pump laser source **101** to receive the pump laser beam at one end and coupled to an optical waveguide **300** at another end. The optical waveguide **300** is configured to receive optical waves of the pump laser beam output from the optical coupler **400** and to transmit the optical waves through gas medium containing a target gas specimen to be measured.

Referring to FIG. **1A** again, a probe laser source **104** for generating a probe laser beam is coupled to the optical waveguide **300** via the optical coupler **400**, allowing the probe laser beam generated to mix with the pump laser beam when being simultaneously transmitted through the gas medium on a path guided by the optical waveguide **300**. The probe laser beam senses the photothermal effects of the target gas specimen and performs a phase shift when propagating through the gas medium in the optical waveguide **300**.

After outputting from the optical waveguide **300**, the pump laser beam of the mixed beams is filtered out by an optical filter **105** coupled to the optical waveguide **300**, while the probe laser beam is transmitted by the optical filter **105** to a combiner **107** that is coupled to the optical filter **105** at one end and is in connection with a local oscillator **108** at another end. The local oscillator **108** provides a light output having a fixed offset Ω in frequency with respect to the frequency of the probe laser **104**.

In one embodiment, both the probe laser source **104** and the local oscillator **108** are continuous-wave (CW) sources, emitting light beams of fixed optical power and of a fixed wavelength absent disturbance.

In FIG. **1A**, the combiner **107** is configured to perfectly align the probe laser beam and the light output from the local oscillator **108**. Further, a photodetector **106** is coupled to the output of the combiner **107**.

As illustrated in FIG. **1B**, the photodetector **106** is configured to capture the probe laser beam **109** from the optical waveguide **300** and the light beam **110** from the local oscillator **108**, generating a beat note **111** at the frequency Ω . As a result, the photothermal phase signal characterizing the target gas specimen is encoded into the phase of the beat note **111**.

In one embodiment, the photodetector **106** is a square-law photodetector for capturing the beat note generated by the probe laser beam **109** transmitted through the optical waveguide **300** and the light beam **110** generated by the local oscillator **108**.

Referring to FIG. **1A** again, the heterodyne interferometric PTS system **100** further comprises a demodulation module **200** coupled to the photodetector **106** to receive the beat note **111** and configured to demodulate the photothermal signals carried by the beat note **111**. The demodulation module **200** additionally receives a signal input from the signal generator **103** to perform the demodulation.

In one embodiment, by demodulating the beat note **111**, one or more characteristics, such as a concentration, a pressure, or a temperature, of the target gas specimen can be thereafter determined.

FIG. **2** is a diagram showing the demodulation module **200** configured for detecting beat note and detecting harmonic components of the photothermal phase signals. The demodulation module **200** comprises a splitter **201**, a first mixer **202** having one input end coupled to one output end of the splitter **201** to receive a first output signal of the splitter **201**, a first reference source **203** having an output end coupled to another input end of the first mixer **202** to provide a first reference signal to the first mixer **202**, a first low pass filter **206** coupled to the first mixer **202** to receive output signals of the first mixer **202**.

The demodulation module **200** further comprises a second mixer **205** having an input end coupled to another output end of the splitter **201** to receive a second output signal of the splitter **201**, a second reference source **204** having an output end coupled to another input end of the second mixer **205** to provide a second reference signal to the second mixer **205**, and a second low pass filter **207** coupled to the second mixer **205** to receive output signals of the second mixer **205**.

The demodulation module **200** additionally comprises a divider **208** having an input end coupled to both the first low pass filter **206** and the second low pass filter **207** to receive outputs of both the first low pass filter **206** and the second low pass filter **207**, a digital arctangent module **209** coupled to an output of the divider **208** to receive output signals of the divider **208**, a third mixer **210** having one input end coupled to an output of the digital arctangent module **209** to receive output signals of the digital arctangent module **209**, and a third reference source **211** coupled to another input end of the third mixer **210** to provide a third reference signal to the third

mixer **210**, and a third low pass filter **212** coupled to an output of the third mixer **210** to receive output signals of the third mixer **210**.

The embodiments of subject invention also provide a gas measuring method comprising following steps.

5 Referring to FIG. 3, at a step **S10**, the light beam **110** is generated by the local oscillator **108** having a frequency shifted by Ω against the optical frequency of the probe laser beam **109** having a phase modulation due to the photothermal effect, and then a beat note signal **111** is generated by the photodetector **106**. At this step, when the pump laser beam at a certain wavelength passes through the gas medium containing the target gas specimen, a portion of the
10 laser power is absorbed when the laser wavelength is in resonance with a specific absorption line of the target gas specimen. When the wavelength and/or intensity of the pump laser beam is modulated at a frequency of f (in kHz), a periodic heating process occurs and subsequently changes the refractive index of the gas medium. The refractive index variation leads to the phase modulation of the probe laser beam that travels along the same path of the pump laser beam in
15 the optical waveguide. The phase signal of the probe laser is relevant to the absorption path length, pump power and absorption coefficient. When these two perfectly aligned plane waves of the probe laser beam **109** and the local oscillator light beam **110** with the frequency difference of Ω are received by the square-law photodetector **106**, a heterodyne beat note **111** at the frequency Ω is generated. It is noted that the phase signal also propagates through the beat note **111**.

20 Then, at a step **S20**, the phase of the beat note signal is demodulated by digital lock-in phase detection. At this step, the beat note **111** is split into two ways. The beat note of the first way is mixed with a first reference signal at the frequency Ω provided by the first reference source **203**. The beat note of the second way is mixed with a second reference signal at a frequency Ω provided by the second reference source **204**. The reference signals generated by the
25 first reference source **203** and the second reference source **204** have a phase difference of 90° . The mixed signal of the first way and the mixed signal of the second way are filtered by the first low-pass filter **206** and the second low-pass filter **207**, respectively.

30 Next, the divider **208** is configured to compare the output signals from the first low-pass filter **206** and the second low-pass filter **207**. The digital arc tangent module **209** is then configured to determine the phase of the beat note signal.

Further, at a step S30, the harmonic signal of the PTS from the phase of the beat note is demodulated by digital lock-in amplitude detection. The signal at frequency f generated from the signal generator 103 is provided as the reference signal for the third reference source 211. At this step, an in-phase reference signal generated by the third reference source 211 is mixed with the beat note phase signal to extract a harmonic component at a frequency which is a multiple of f , such as f , $2f$, or $3f$. The first harmonic ($1f$) and second harmonic ($2f$) signals are provided for gas measurement. The third low-pass filter 212 is configured to eliminate high-frequency components of the mixed signal output from the third mixer 210.

Referring to FIG. 4A, the core-cladding-mode interference PTS system 500 comprises the same components and arrangements of the pump laser source 101, the laser driver 102, the signal generator 103, the probe laser source 104, the optical coupler 400, the optical waveguide 300, and the optical filter 105, included in the heterodyne PTS system shown in FIG. 1A.

In FIG. 4B, when the probe laser source 104 is coupled to the waveguide 300, a portion of the probe light enters the cladding region while another portion of the probe light enters the core region of the waveguide 300. The spectral transmission of the probe laser inside the waveguide 300 includes the interference between the core mode 502 and cladding mode 503.

Referring to FIG. 4A again, the core mode 502 and cladding mode 503 both propagate along the waveguide 300, but meeting different refractive index values, leading to a mode interference at the fiber output which is detected by the photodetector 106. The photodetector signal is analyzed by a lock-in amplifier 501 with the reference signal generated from the signal generator 103 for the first ($1f$) or second harmonic ($2f$) detection. The harmonic signals of the mode interference output provide information such as the concentration, the pressure or the temperature of the gas specimen.

Compared to the conventional active homodyne detection method, the passive phase detection of photothermal signal generated according to the embodiments of the subject invention does not require active stabilization of the quadrature point of the interferometer, significantly simplifying the sensor configuration and eliminating the electronic noises caused by the piezoelectric actuator.

Moreover, in the embodiments of the subject invention, the local oscillator 108 is configured to down-convert the optical frequency to RF which can be readily analyzed by a high-speed lock-in amplifier. Since the phase detection process normalizes the amplitude

components, the resultant signal has an intrinsic immunity to the amplitude variation of the heterodyne photocurrent, offering advantages when there is a change of the heterodyne amplitude caused by the unavoidable power and polarization variation. It is known that a strict power balance and polarization control between the two arms of an interferometer is required in homodyne detections. Any amplitude fluctuation of the homodyne signal may cause the reset of the stabilization circuit or signal fading issues.

Now referring to FIGS. 5A-5C in which various configurations of the optical waveguide 300 of the PTS system 100 can be employed for light beam transmissions and light-gas interactions.

In one embodiment, as shown in FIG. 5A, the optical waveguide 300 can be implemented by an inner-coating hollow core fiber 301. The inner-coating hollow core fiber 301 is formed to have a tubular shape, comprising a protection layer 302 made of a material such as glass or plastics, a reflective coating layer 303 made of a material such as silver, a dielectric coating layer 304 made of a material such as silver iodide, and a hollow core region 305 filled with gas medium containing the target gas specimen to be measured.

In one embodiment, the hollow core region 305 can be configured to have a diameter in a range of 200-500 microns and to extend along a longitudinal axis of the inner-coating hollow core fiber 301. Light beams are configured to travel inside the hollow core region 305. Moreover, the inner-coating hollow core fiber 301 may have a spectral transmission window in a range between 2 microns and 16 microns.

Referring now to FIG. 5B, in another embodiment of the subject invention, the optical waveguide can be implemented by a hollow-core anti-resonant fiber 310. The fiber 310 is formed to have a tubular shape, comprising a hollow core region 315 and a cladding layer 311. The cladding layer 311 can be configured to have an outer cladding layer 312 and an inner cladding layer 313; a single ring of capillaries 314 can be configured to make up the inner cladding layer 313, and a small gap is left between two adjacent capillaries 314. The cladding layer can be made of, for example, silica and soft glass materials. The hollow core region 315 extends along the longitudinal axis of the hollow-core anti-resonant fiber 310 and may have a diameter in a range of 50-100 microns, surrounded by 6-8 capillaries. The light beams are configured to travel inside the hollow core region 315.

In addition, as illustrated in FIG. 5C, in another embodiment of the subject invention, the optical waveguide can be implemented by a slot waveguide 320. A slot waveguide comprises a first strip 321 and a second strip 322 of high-refractive-index materials separated by a sub-wavelength-scale low-refractive-index slot region 323. The first strip 321 and the second strip 322 are disposed on a substrate 324. A portion of the guided light is located in the slot region 323 by the means of evanescent wave. The high-refractive-index material can be silicon, silicon nitride, lithium niobate or chalcogenide. The low-refractive-index slot region 323 is filled with gas medium having the gas species to be detected. Compared with fiber-optic gas sensors, the slot waveguide has the advantage of monolithic integration, allowing providing the integrated sensing element, the laser source and the photodetector on a single chip.

Referring to FIGS. 6A-6B, various configurations of the optical coupler 400 of the PTS system 100 can be employed for light beam transmissions and light-gas interactions.

In one embodiment, as shown in FIG. 6A, the optical coupler 401 comprises a first lens 402, a dichroic mirror (or beam splitter) 403, and a second lens 406. The optical coupler 401 is configured to couple the pump laser beam 407 and probe laser beam 405 to simultaneously propagate through the optical waveguide 300. The pump laser beam 407 of the pump laser source 101 passes through the first lens 402 and the dichroic mirror 403 and then illuminates onto the facet of the optical waveguide 300 which is placed at the focal point of the first lens. The collimated beam 405 of probe laser source 104 passes through the second lens 406 and is reflected at the dichroic mirror 403 and then illuminates onto the facet of the optical waveguide 300 which is placed at the focal point of the second lens 406. The dichroic mirror 403 is configured to have high transmission rate at the wavelength of the pump laser while having high reflectivity at the wavelength of the probe laser. The free-space optical coupling can be configured for optical waveguide 300 of any dimensions by matching the focus spot size of the first lens and the second lens with the mode field diameter of the optical waveguide 300.

Referring now to FIG. 6B, in another embodiment of the subject invention, the coupler 400 can also be implemented by a fiber-optic coupler 410. The fiber coupler 410 comprises a first input fiber 411 and a second input fiber 412. The first input fiber 411 is connected to the probe laser; the second input fiber 412 is connected to the pump laser. The laser beams from the input ends are combined and launched into the common output fiber 413, which is connected to the optical waveguide 300. It is noted that two or more pump lasers could be adopted to realize

multi-species detection, by selecting appropriate pump wavelengths for specific gas species and connecting the n^{th} ($n > 1$) pump laser to the n^{th} input fiber **414** of the coupler **410**. The coupler **410** can be butt-coupled or fusion spliced to the waveguide **300**.

FIG. **7** is a plot diagram of representative photothermal $1f$ signals measured by the heterodyne interferometric PTS system shown in FIG. **1A** under different concentrations of N_2O (0%, 0.91%, 1.4% and 1.8%) gas diluted by N_2 gas. A continuous-wave interband cascade laser emitting at $3.6 \mu\text{m}$ is used as the pump laser that is tuned across the absorption line-center of the target gas N_2O at 2778.37 cm^{-1} . The first harmonic ($1f$) signal is retrieved by setting the third reference source **211** to the frequency f ; higher order harmonic signals can be retrieved by simply setting the third reference source **211** to a frequency that is a multiple of f , such as f , $2f$, or $3f$. The signal amplitude is determined to be changed linearly with the N_2O concentration. It is noted that the application of the subject invention is not limited to N_2O detection. By selecting appropriate pump lasers for specific species, different types of gas molecules can be detected by the embodiments of the subject invention.

FIG. **8B** is a plot diagram of continuous monitoring of the first harmonic of photothermal signals for the scanned PTS- $1f$ signal (9 periods) under the condition of the simultaneous power fluctuation of the probe laser beam shown in a plot diagram of FIG. **8A**. The PTS signal is not affected by any disturbance of the probe light beams. In other embodiments, the power immunity are also be realized in other harmonic detections.

FIG. **9** is a plot diagram of representative photothermal $2f$ signals measured by the core-cladding-mode interference PTS system shown in FIG. **4A** under different concentrations of NO (0-100 ppm) gas diluted by N_2 gas. A continuous-wave quantum cascade laser emitting at $5.2 \mu\text{m}$ is used as the pump laser that is tuned across the absorption line-center of the target gas NO at 1900.08 cm^{-1} . The signal amplitude is determined to be changed linearly with the NO concentration.

The pump-probe PTS system and methods of the subject invention employ phase-sensitive detection techniques to achieve easier retrieval of photothermal phase signals that is immune from power fluctuation and thus can be utilized for gas sensing without requiring active stabilization. Moreover, optical waveguides that contain gas medium having the target gas specimen is coupled with the PTS system, allowing real-time retrieval of the photothermal phase signal for gas measurements. Various optical waveguide configurations, including but not

limited to, hollow-core fibers, or planar waveguides, can be implemented to decrease the dimensions of optical waveguide sensors while increasing the light-specimen interaction duration for higher photothermal efficiencies.

All patents, patent applications, provisional applications, and publications referred to or
5 cited herein are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this
10 application and the scope of the appended claims. In addition, any elements or limitations of any invention or embodiment thereof disclosed herein can be combined with any and/or all other elements or limitations (individually or in any combination) or any other invention or embodiment thereof disclosed herein, and all such combinations are contemplated with the scope of the invention without limitation thereto.

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CLAIMS

We claim:

1. A system for gas measurements based on pump-probe photothermal spectroscopy (PTS) with passive phase detection, the system comprising:

a pump laser source generating a pump laser beam propagating through a target gas specimen, a wavelength of the pump laser beam being tuned around absorption characteristics of the target gas specimen to be measured;

an optical waveguide configured to transmit the pump laser beam through a gas medium containing the target gas specimen to be measured;

an optical coupler coupling the pump laser source with the optical waveguide;

a laser driver configured to control temperatures and injection currents of the pump laser source;

a signal generator connected to the laser driver and configured to provide modulation to the pump laser source;

a probe laser source configured to generate a probe laser beam connected to the optical coupler and coupled to the optical waveguide;

an optical filter connected to an output of the optical waveguide and configured to filter out the pump laser beam and to transmit the probe laser beam;

a local oscillator configured to generate a local oscillator light;

a combiner connected to the local oscillator and an output of the optical filter and configured to align the local oscillator light with the probe laser beams output from the optical filter;

a photodetector connected to the combiner and configured to generate beat notes when the probe laser beams and local oscillator light are simultaneously received by the photodetector; and

a demodulation module connected to the photodetector and configured to detect and measure a photothermal phase signal based on the beat notes received from the photodetector for gas measurements.

2. The system of claim 1, wherein the local oscillator provides continuous-waves that have a fixed frequency shift with respect to a frequency of the probe laser.

3. The system of claim 1, wherein the probe laser beam and the pump laser beam are mixed when propagating through the optical waveguide.

4. The system of claim 1, wherein the optical waveguide is a slot waveguide disposed in the target gas specimen.

5. The system of claim 4, wherein light propagating through the slot waveguide generates a portion of an evanescent field on the target gas specimen.

6. The system of claim 1, wherein the modulation of the pump laser source is wavelength modulation and/or amplitude modulation and has a frequency in a scale of kHz.

7. The system of claim 1, wherein the probe laser beam is configured to have a phase shift when propagating through the waveguide.

8. The system of claim 7, wherein the photothermal signal includes harmonics of the phase shift and has a linear relationship with a gas concentration of the target gas specimen.

9. The system of claim 1, wherein the demodulation module comprises a splitter, a first mixer, a first reference source, a first low pass filter, a second mixer, a second reference source, a second low pass filter, a divider, a digital arctangent module, a third mixer, a third reference source, and a third low pass filter.

10. A method based on heterodyne interferometric PTS that demodulates photothermal signals for gas measurements, the method comprising:

providing light beams, by a local oscillator, having a frequency shifted against an optical frequency of a probe laser beam having a phase modulated under a photothermal effect;
generating, by a photodetector, beat note signals;
demodulating, by a digital lock-in phase detector, phases of the beat note signals; and

demodulating, by a digital lock-in amplitude detector, harmonic signals of PTS from the demodulated phases of the beat note signals for gas measurements.

11. The method of claim 10, further comprising splitting the beat note signals into first and second beat note signals, mixing the first and second beat note signals with an in-phase reference signal and a quadrature reference signal, respectively, and transmitting the first and second beat note signals that are mixed with corresponding reference signals through first and second low pass filter, respectively.

12. The method of claim 10, wherein the phases of beat note are determined by a digital arc tangent method.

13. The method of claim 10, wherein the beat note signals are mixed with a reference at a frequency equal to kf , where k is a positive integer, and transmitting through a LPF.

14. A method based on core-cladding-mode interference PTS that demodulates photothermal signals for gas measurements, the method comprising:

generating, by coupling the probe light to a cladding region and a core region of a waveguide, a core mode and a cladding mode simultaneously;

generating, by a photodetector, mode interference signals;

demodulating, by a digital lock-in amplifier, the harmonic signals from a mode interference output.

15. The system of claim 1, wherein the optical waveguide is an inner-coating hollow core fiber.

16. The system of claim 1, wherein the optical waveguide is a hollow-core anti-resonant fiber.

FIG. 1A

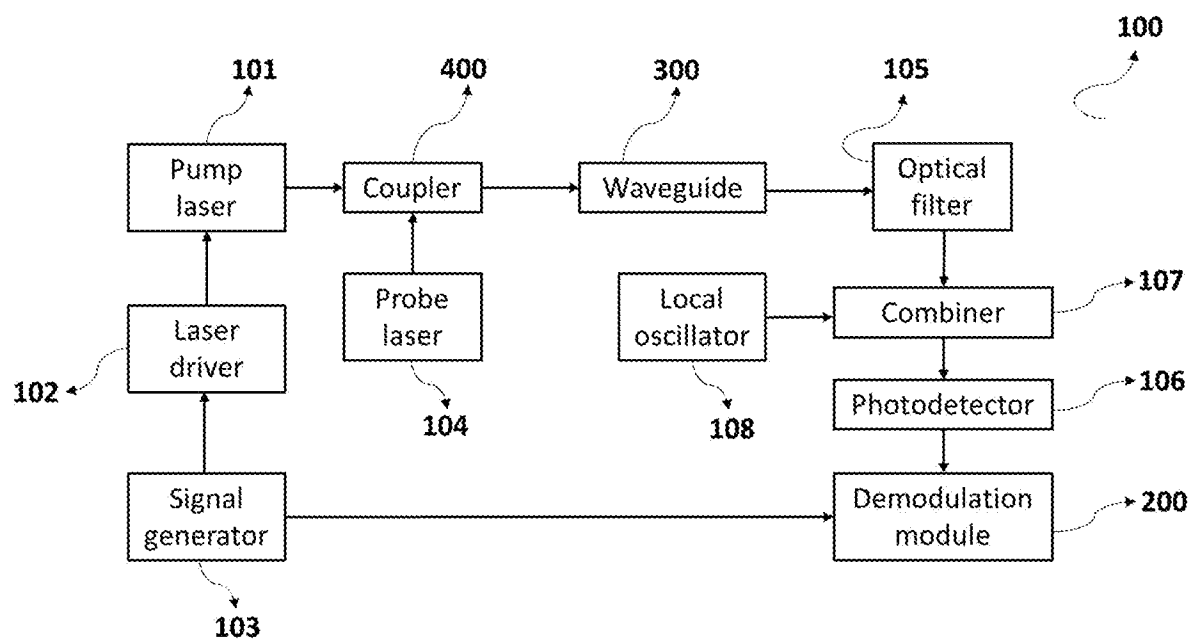


FIG. 1B

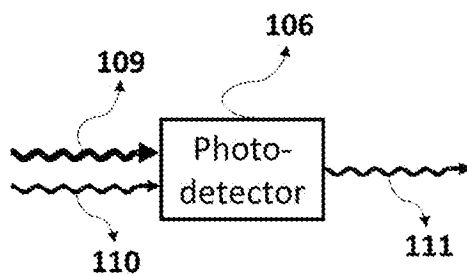


FIG. 2

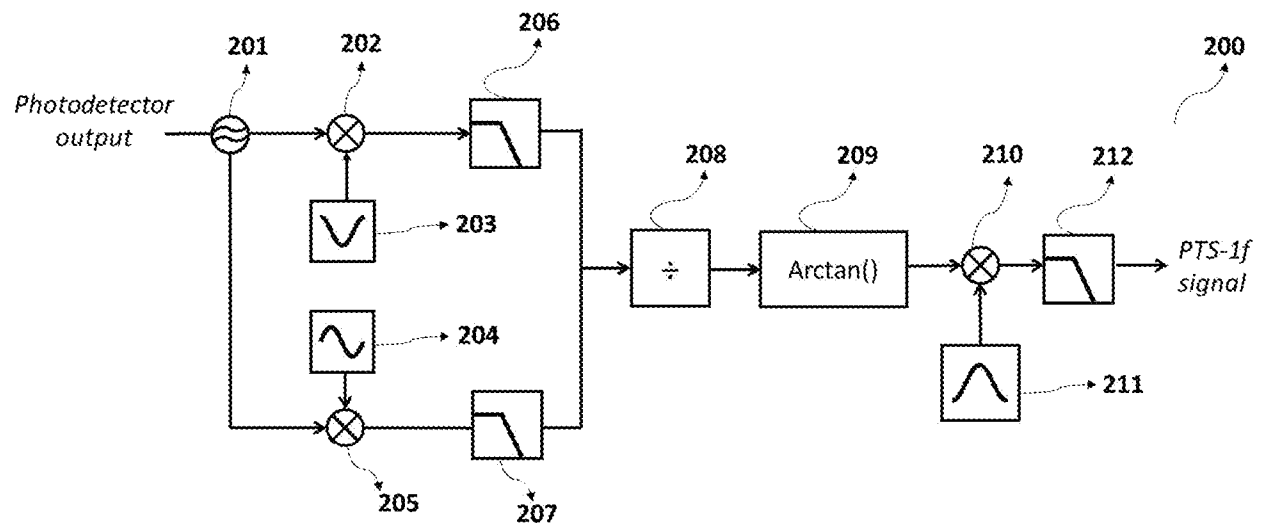


FIG. 3

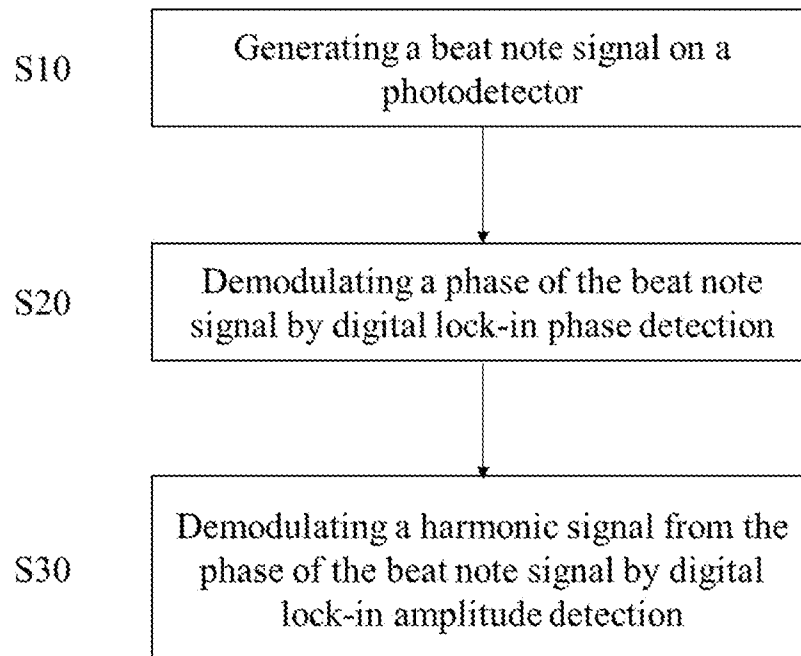


FIG. 4A

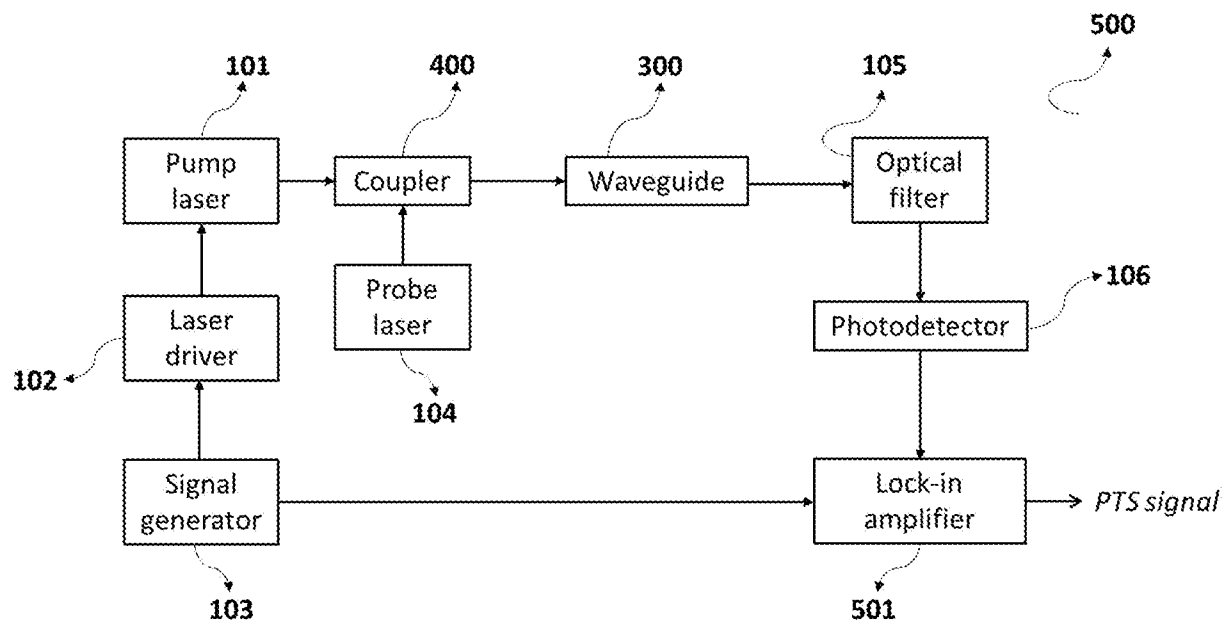


FIG. 4B

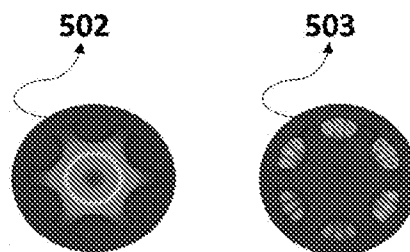


FIG. 5A

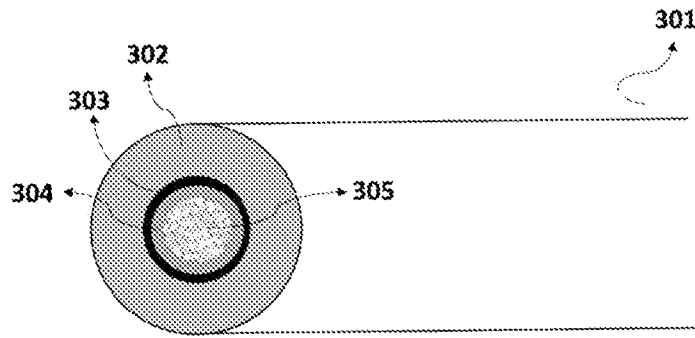


FIG. 5B

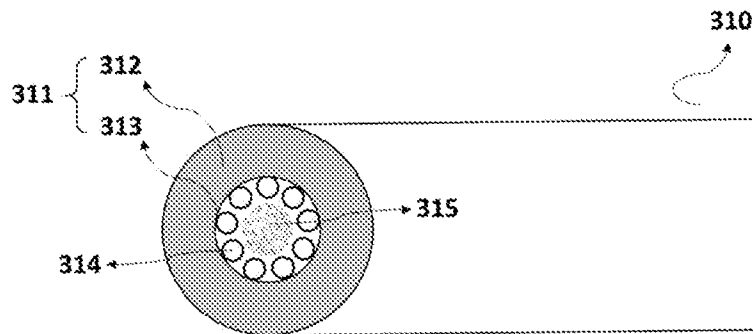
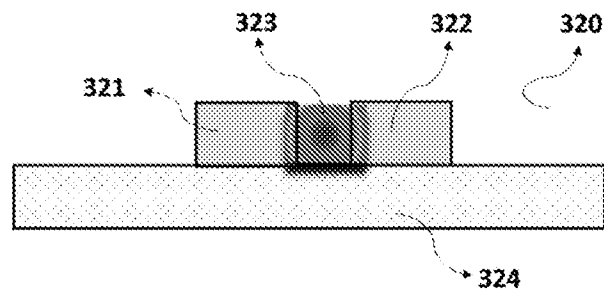


FIG. 5C



300

FIG. 6A

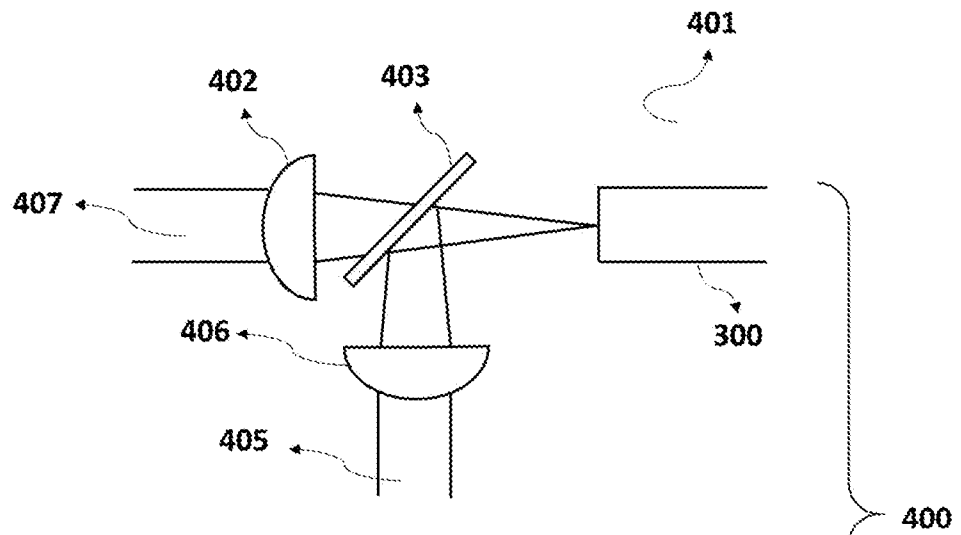


FIG. 6B

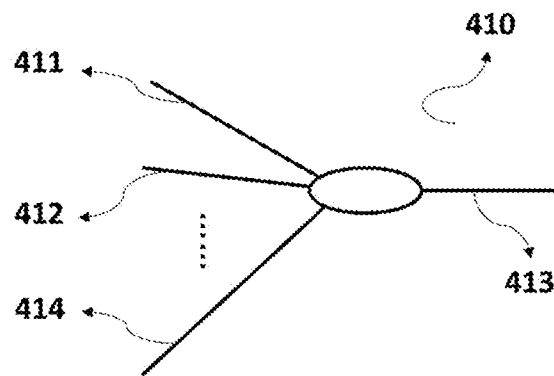


FIG. 7

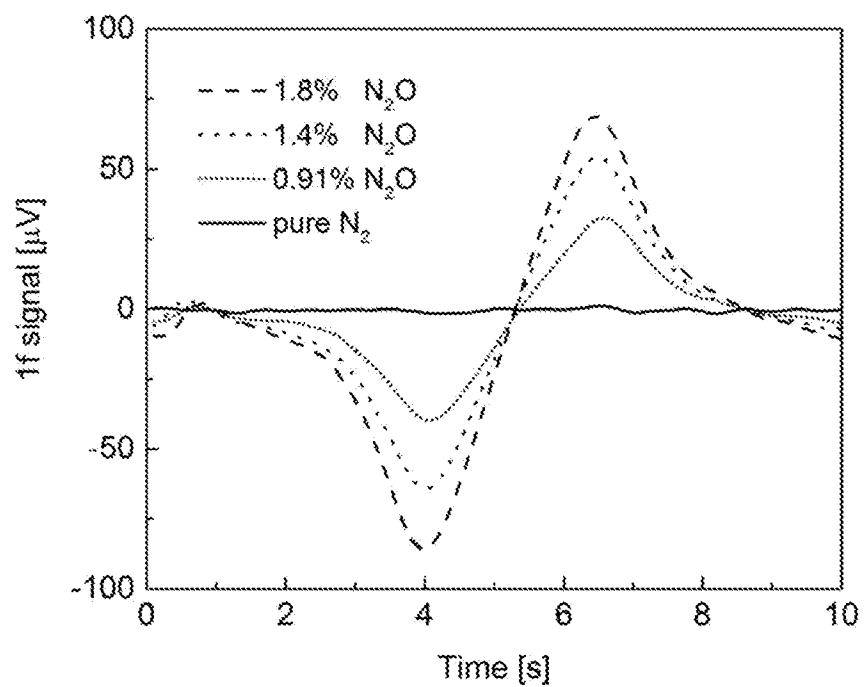


FIG. 8A

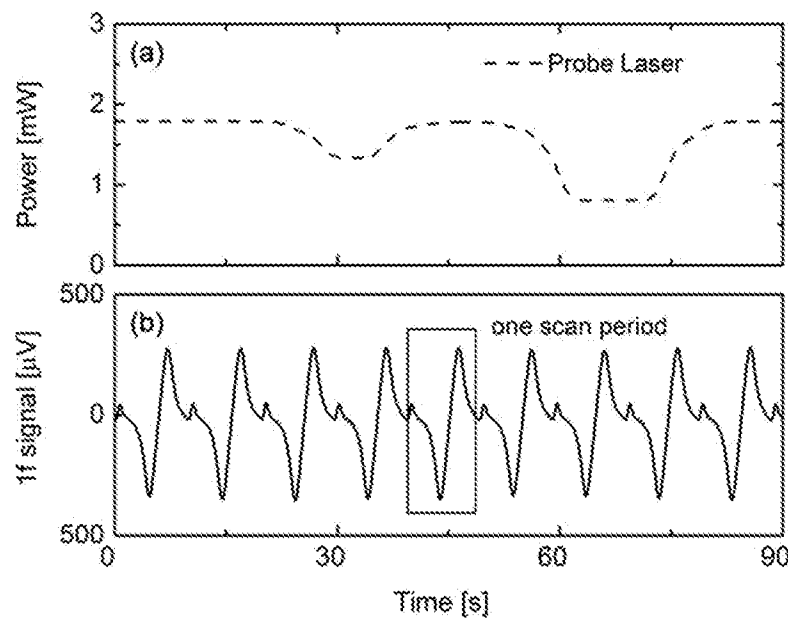
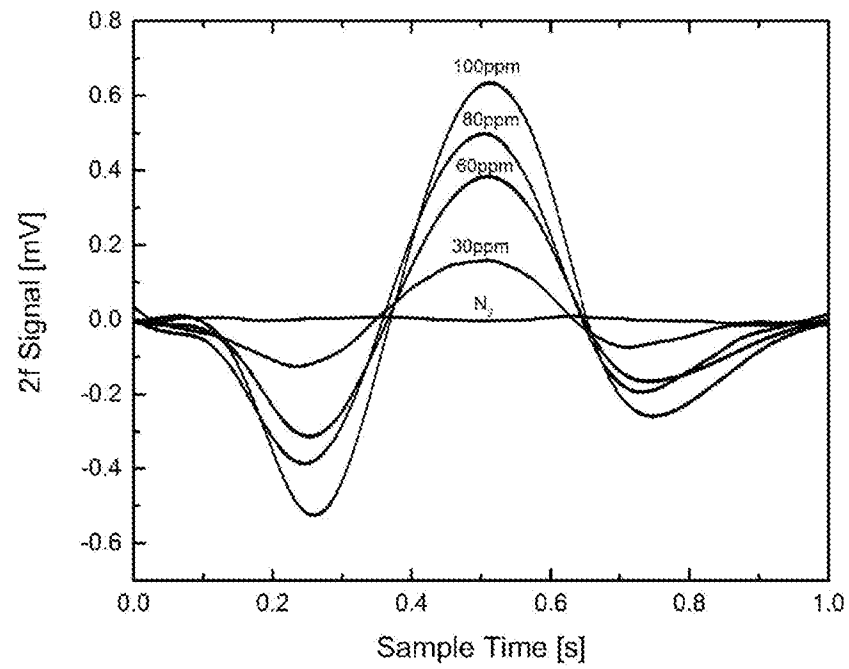


FIG. 8B

FIG. 9



INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2022/102690

A. CLASSIFICATION OF SUBJECT MATTER

G01N 21/63(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G01N21/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT, CNKI, WPI, EPODOC: PTS, gas, measure, detect+, sens+, photothermal spectroscopy, laser, light, source, beat, interfer+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 104596996 A (SHENZHEN RESEARCH INSTITUTE, THE HONG KONG POLYTECHNIC UNIVERSITY) 06 May 2015 (2015-05-06) description, paragraphs 0006-0048, figures 1-2	1-13
Y	CN 104596996 A (SHENZHEN RESEARCH INSTITUTE, THE HONG KONG POLYTECHNIC UNIVERSITY) 06 May 2015 (2015-05-06) description, paragraphs 0006-0048, figures 1-2	14-16
Y	CN 110726697 A (SOUTH CHINA NORMAL UNIVERSITY) 24 January 2020 (2020-01-24) description, paragraphs 0021-0038, figure 1	14-16
A	CN 103175807 A (NANJING UNIVERSITY) 26 June 2013 (2013-06-26) the whole document	1-16
A	US 2005105099 A1 (SHPANTZER, Isaac et al.) 19 May 2005 (2005-05-19) the whole document	1-16
A	CN 112683876 A (CHONGQING UNIVERSITY, et al.) 20 April 2021 (2021-04-20) the whole document	1-16
A	CN 110098556 A (SHANGHAI INSTITUTE OF TECHNICAL PHYSICS, CHINESE ACADEMY OF SCIENCES) 06 August 2019 (2019-08-06) the whole document	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

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“O” document referring to an oral disclosure, use, exhibition or other means

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“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

06 September 2022

Date of mailing of the international search report

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Telephone No. 86-(10)-53962412

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2022/102690

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
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CN	110726697	A	24 January 2020	None			
CN	103175807	A	26 June 2013	CN	103175807	B	17 June 2015
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				CA	2587460	A1	04 January 2007
				EP	1836453	A2	26 September 2007
				AU	2002258444	A1	07 April 2003
				WO	2007001379	A2	04 January 2007
				US	7277178	B2	02 October 2007
				CA	2587460	C	08 February 2011
CN	112683876	A	20 April 2021	CN	112683876	B	10 May 2022
CN	110098556	A	06 August 2019	None			