Optically Driven Nano-Beam Resonator for Hydrogen Sensing

Wei Ding, Shen Liu, Peijing Chen, Bonan Liu, Hang Xiao, Xin Ding, Ying Wang, and Yiping Wang, *Senior Member, IEEE*

***Abstract*—We introduce a hydrogen sensor based on a beam-structured optomechanical resonator engraved by the FIB (focused ion beam) in a graphene-Au-Pd nanofilm, suspending on the tip of the optical fiber. The hydrogen concentration can be measured by monitoring the resonance frequency change which attribute to the mechanical stress changes associated with hydrogen. The sensor responds linearly in a wide concentration range of from 0 to 4.5%. The sensitivity of proposed sensor can be calculated to be 95.7 kHz/% with a shift of 445.11 kHz. Due to its excellent repeatability in the measurement process, such a sensor may be used practically for hydrogen gas with high concentrations.**

***Index Terms*—Hydrogen sensor, optical fiber sensor, optomechanical resonator.**

I. Introduction

HYDROGEN as a clean, efficient and renewable energy source has been widely used in various fields such as aerospace [1], automotive [2], electronics and petrochemicals [3]. In nature, 4%-4.5% of hydrogen can explode when exposed to a spark, causing major safety accidents and threatening the safety of people and property [4]. Hydrogen monitoring is of great significance in various domains since it affects humans negatively as well as favorably. To achieve this goal, in the past few decades, a range of sensors have been developed based on electrochemical [5], microelectromechanical resistive [6], and optical mechanisms [7]. Fiber-optic hydrogen sensors have gained more attention than commercial hydrogen sensors with electronic sensing elements due to their inherent benefits, including the capability to prevent electromagnetic interference, minimal safety hazards and ability to perform remote measurements. Among these sensors, Palladium (Pd) is frequently used as the catalyst with a high affinity towards H_2 and great reversible absorption of hydrogen, leading to the formation of palladium hydride (PdH_x). PdH_x can exist in two distinct solid phases, α- and β-hydride, which depend on the hydrogen content, temperature and pressure. When the Pd in the coating comes into contact with hydrogen, the Pd cover layer expands in volume and stretches the fiber, resulting in changes in the parameters of the optical signal and thus reflecting changes in hydrogen information, which has the advantage of a large measurement range and high sensitivity.

Mechanical modes of resonators can be driven using electrical methods by Micro- and Nano-electromechanical systems (MEMS and NEMS). These resonators have shown tremendous potential in the detection of mass [8], [9], force [10], [11], gas [12] and magnetic [13]. Nevertheless, the described mechanism has several associated drawbacks, such as nonlinear output, short circuit potential, and the need for a high drive voltage. Optical driving based on modulating optical power coupled directly to the resonator have been proposed as an effective approach to address above problems. Numerous mechanical resonators have been developed for sensing purposes, utilizing optical driving and readout systems. These resonators include optomechanical magnetometers [14], [15], optomechanical accelerometers [16], and displacement sensors [17], [18].

In this paper, supported by our previous works [4], [19], [20], A fiber-optic hydrogen sensor with a novel structure is proposed and experimentally investigated. The fiber-optic Fabry-Perot interferometer was fabricated by splicing a short hollow-core fiber (HCF) to a single-mode fiber (SMF). The end face was then sensitized by using a beam-shaped mechanical resonator, which was made of a layered graphene-Au-Pd nanofilm. For analysis of mechanical vibration, a sine-sweep modulated laser was used for actuation while a continuous wave laser was used for detection. The experiment revealed that Pd films could convert lattice expansion into metal hydride when exposed to hydrogen reversibly, which leads to frequency shifts. Accurate determination of hydrogen concentration was achieved through measurement of the shift in resonance frequency. The sensing platform is solely constructed from integrated optical fibers, with all-optical components for actuation and measurement, making it highly resistant to any electromagnetic interferences.

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The authors are with the Shenzhen Key Laboratory of Photonic Devices and Sensing Systems for Internet of Things, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China, and also with the Guangdong and Hong Kong Joint Research Centre for Optical Fiber Sensors, Shenzhen University, Shenzhen 518060, China (e-mail: 2110456062@email.szu.edu.cn; shenliu@szu.edu.cn; 2070456073@email.szu.edu.cn; ssamliu@163.com; 2060453045@email.szu.edu.cn; danielxin2019@126.com; yingwang@szu.edu.cn; ypwang@szu.edu.cn).

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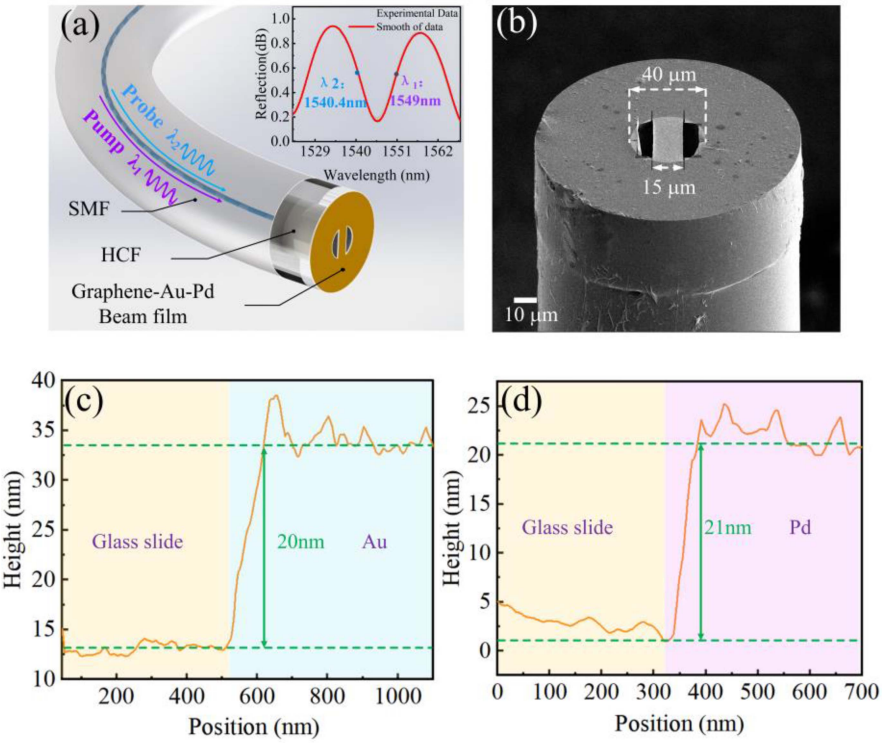

Fig. 1. (a) Structure schematic diagram of the proposed hydrogen sensor. Inset: Reflection spectrum of Graphene-Au-Pd nanofilm Fabry-Perot interferometer. (b) SEM image of the beam-film resonator. (c) The height profile of Au film. (d) The height profile of Pd film.

II. Sensor Fabrication and Principle

Fig. 1(a) is the structure schematic of the proposed sensor. A Fabry-Perot interferometer (FPI) is formed by the beam-shape composite film and the end face of the SMF. The reflection spectrum is provided in the inset. Its fabrication involves several steps. Firstly, a section of HCF with an internal diameter of 40 μm was fused to an SMF end face using a commercial fusion splicer. The HCF used had a well-cleaved end face and a length of 30–50 μm which contributes to low insertion losses. Secondly, a wet transfer technique was employed to transfer a multilayer graphene membrane to the end of HCF. The suspended graphene was then coated with a layer of Au film via magnetron sputtering to enhance the reflectivity. Then, a beam shape was carved into the suspended film by employing FIB technique. Fig. 1(b) displays the beam-shape diaphragm by the SEM (scanning electron microscope), fabricated to be approximately 40 μm in length and 15 μm in width. Finally, a Pd film was deposited onto the graphene-Au beam diaphragm for hydrogen sensing. As shown in Fig. 1(c), (d), the thickness of gold film and Pd film was characterized by atomic force microscope (AFM) to be 20 nm and 21 nm, respectively.

The Pd on the beam-film undergo lattice expansion during reversible hydrogenation, which leads to a frequency shift in spectrum. Upon hydrogen release, the stationary regions of the beam-film minish, exerting longitudinal compressive stress on the suspended graphene-Au-Pd film and leading to decreased resonance frequencies. For a beam-film with a length of L and a thickness of t, its fundamental resonant frequency f_0 can be expressed as [21]

$$f_0 = \sqrt{\left(A\sqrt{\frac{E}{\rho}}\frac{t}{L^2}\right)^2 + \frac{0.57A^2S}{\rho L^2 t}} \tag{1}$$

The E and ρ denote the Young's modulus and mass density of the beam, respectively. The S stands for the tension per unit width of the beam, while A takes the value of 1.03. The relative variation of the resonant frequency can be expressed as follows [12]:

$$\frac{\Delta f}{f_0} \approx -0.1475\left(\frac{\sigma}{E}\right)\left(\frac{L}{t}\right)^2 \tag{2}$$

where, σ denotes the longitudinal tensile stress in the composite film, L represents the length and t represents the thickness. E is the Young's modulus of the material.

III. Hydrogen Measurement and Discussion

The experimental setup is illustrated in Fig. 2. An optical spectrum analyzer (OSA), a broadband source (BBS), and a circulator were used for measuring the FPI spectrum at port 1. The hydrogen concentration control setting is shown on the right side of Fig. 2. Compressed nitrogen and hydrogen generator were supplied, with the volume ratio being regulated by two gas mass flow controllers (MFC) and a personal computer (PC). The full control range for nitrogen flow control and hydrogen flow control is 1000 SCCM (standard cubic centimeters per minute) and 500 SCCM, respectively. A mixture of nitrogen and

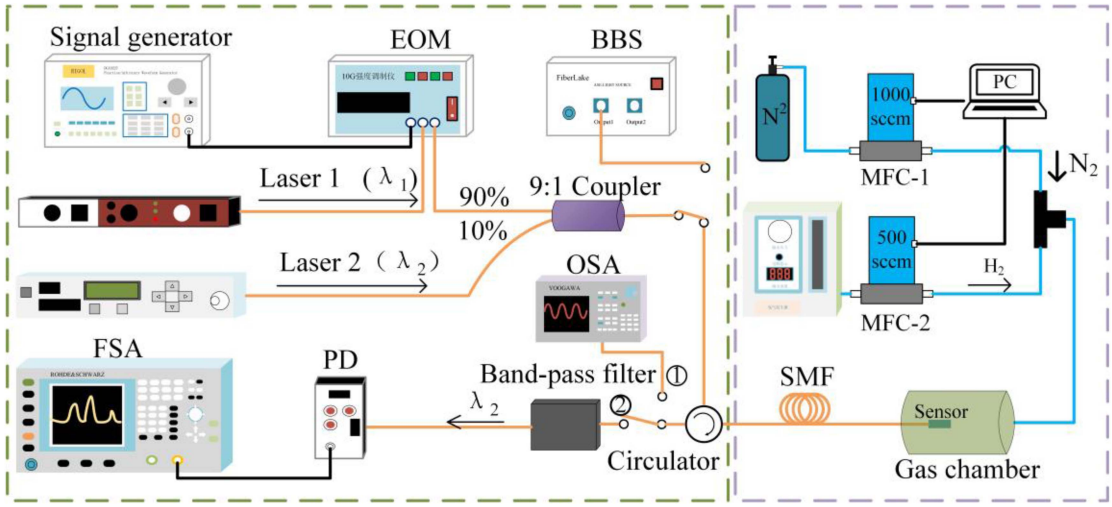

Fig. 2. Schematic of the experimental setup. The sensor's spectral and mechanical frequency characteristics are measured through port 1 and port 2, respectively. The hydrogen concentration is controlled using the right side of the device.

hydrogen with a specific volume ratio flowed through a plastic pipe (inner diameter of 3 mm) into a gas chamber. A proposed sensor was placed on the plastic tube to monitor the variation of hydrogen concentration. During the experiment, a constant total gas flow of 1000 SCCM was maintained. The sensor is a mechanical resonator that can be driven and measured via port 2: The laser wavelength λ_1 was modulated using an electro-optic modulator (EOM) with a center wavelength of 1549 nm, and driven by a sine-sweep signal with a frequency ranging from 10 kHz to 3000 kHz. The modulated λ_1 transmitted through a 9:1 coupler and circulator to reach the FPI, where it actuated the Graphene-Au-Pd film to generate mechanical vibration. The probe laser wavelength λ_2 was set to 1540.4 nm, which was close to the half-maximum of the optical resonance (see Fig. 1(a) inset). Upon passing through the coupler and circulator, laser wavelength λ_2 was reflected by the composite film, and was subsequently detected by a photoelectric detector (PD) while λ_1 was blocked by the bandpass filter. The Nano-film resonator, through its opto-mechanical vibration, was able to modulate the phase difference between the reflected beam of light from the optical fiber end face and the thin-film, thus modulating the reflected light intensity of λ_2. The obtained signal was further analyzed via a frequency spectrum analyzer (FSA) to determine the frequency properties of the optomechanical Nano-film resonator. The hydrogen concentration used during the experiment ranges from 0% to 4.5%.

Fig. 3 shows the mechanical frequency properties of the optomechanical resonator. Two mechanical resonant modes were observed in the range of 1200 kHz $\sim$ 2100 kHz including the fundamental resonant mode (@1472.4 kHz) and the second-order resonant mode (@1871.6 kHz). The vibration modes of the two modes were simulated using COMSOL Multiphysics. It should be noted that the Q-value of the first-order resonant frequency under this structure is significantly higher than that of the previous trampoline structure [18]. The energy magnitude

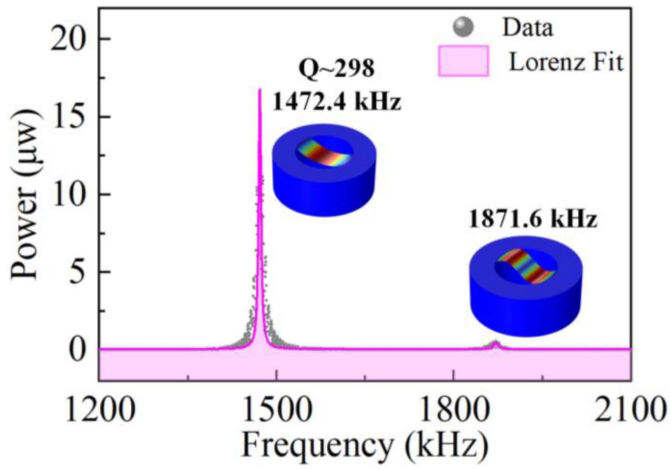

Fig. 3. Mechanical resonant frequency characteristics of the proposed sensor. The vibration mode of the first-order, second-order resonance at 1472.4 kHz and 1871.6 kHz, obtained by finite element simulation is represented, respectively; Inset: Enlarge view of the second-order resonant peak.

of the resonant peak in the second-order mode is below 1 μw. The leading reason of this phenomenon may be attributed to the gradual energy loss suffered by the light passing through the cavity, due to several factors such as absorption, scattering, and miscellaneous losses.

By varying the hydrogen concentration at 22 °C, the frequency response of the sensor was measured. Each measurement was performed after a 5-minute period to reach absorption equilibrium. The frequencies of the two modes decrease as the concentration rises. Fig. 4(a) shows the spectral evolution of the fundamental mode with the hydrogen concentration increasing from 0% to 4.5%. For clarity, the shift of the two modes with the hydrogen concentration is shown in Fig. 4(b). The fundamental mode and the second-order mode exhibited a blue shift of 445.11

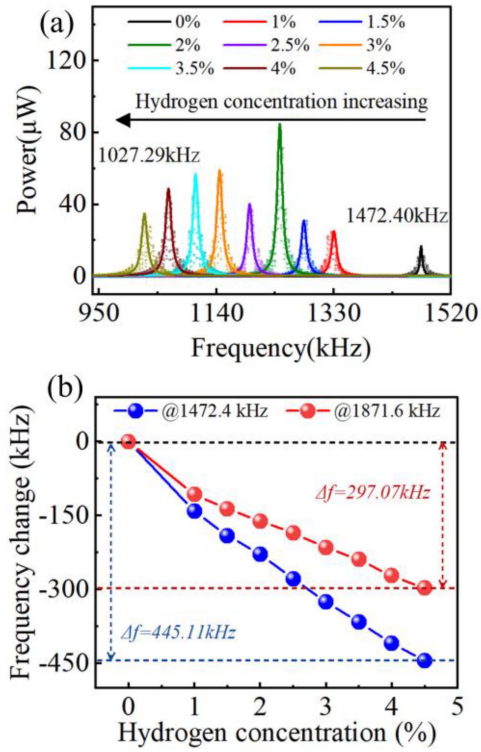

Fig. 4. (a) Spectral evolution of the fundamental mode with hydrogen concentration; (b) frequency shifts of the two modes versus hydrogen concentration.

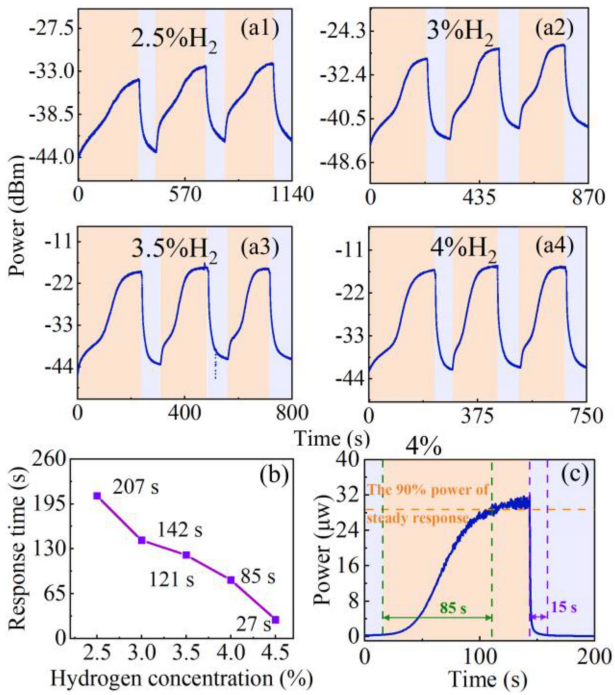

Fig. 5. (a1)–(a4) Several cycles of recording the real-time power response of the sensor exposed to different hydrogen concentrations; (b) temporal response at the hydrogen concentration of 1%; (c) the response time varies with hydrogen concentrations.

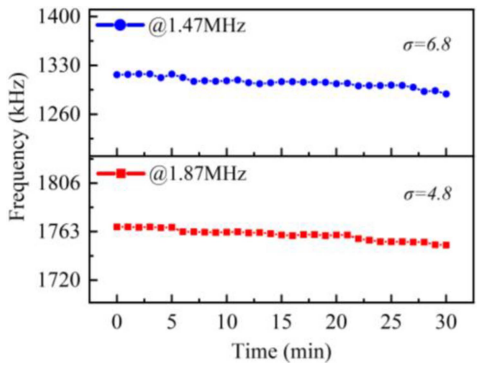

Fig. 6. Fluctuations in resonant frequencies of two modes at 1% hydrogen concentration.

kHz and 297.07 kHz, respectively, during the process. The responses of the two modes are both linear, which are different from the previous trampoline structure [19]. The sensitivities are calculated to be 95.7 kHz/% for the fundamental mode and 61.6 kHz/% for the second-order mode.

In order to evaluate the reproducibility of the proposed hydrogen sensor, light power changes for three cycles at varying concentrations were recorded. As presented in Fig. 5(a1)–(a4), the areas marked by orange and purple indicate that the sensor was exposed to hydrogen and pure nitrogen, respectively. The response time and recovery time are defined as the time needed for 90% of steady-state response to be reached. Fig. 5(c) depicts the temporal response at 4% hydrogen concentration where its response time and recovery time were 85 s and 15 s respectively. Hydrogen atoms occupy more surface sites of Pd at concentrations above 1%, and as a result, the response time is further delayed when exposed to high levels of H_2.

The lower limit detection (LOD) of the proposed hydrogen sensor can be evaluated by detecting the fluctuation of resonant frequency over time. In order to record the frequency fluctuations of two resonant frequencies at 1% hydrogen concentration, we used a PC to control the FSA operation, recording on average once a minute for half an hour. The Fig. 6 represents the resonant frequency fluctuations results obtained by searching for peaks through Lorentz fitting of the experimental data [22]. The fluctuation in frequency could be attributed to the formation of blisters in the palladium film at hydrogen concentration of 1%, which may cause plastic deformation of the palladium film. The standard deviations (σ) of the frequency fluctuations of the two modes were 6.8 kHz, 4.8 kHz, respectively. The 1σ-LODs of the two modes were 710 ppm and 770 ppm by calculation.

In order to investigate the effect of longitudinal tensile stress mentioned above on the thin film, a simulation was conducted using COMSOL Multiphysics. The simulations utilized the standard parameters as follows: a density of graphene at 233.33 kg/m^3, Young's modulus at 1000 GPa, and Poisson's ratio at 0.186 [23]. A horizontal pre-stress was applied to the film, followed by a gradually increasing longitudinal tensile stress, the results were illustrated in Fig. 7. The longitudinal tensile stress change ranging from 0.1 to 0.2 N/m causes a decline in the resonant frequency of resonator.

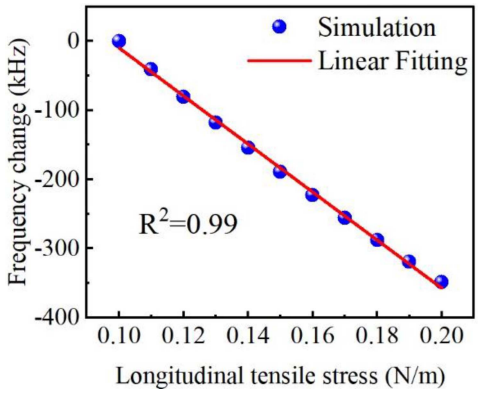

Fig. 7. Relationship of frequency change with longitudinal tensile stress obtained from COMSOL simulations.

IV. Conclusion

In conclusion, an all-optical optomechanical nano-resonator based hydrogen sensor is proposed. The experimental results show that as the hydrogen concentration varied from 0 to 4.5%, linear shifts of 445.11 kHz and 297.07 kHz occurred in the fundamental and second resonant frequencies, respectively. The hydrogen sensitivity of the resonator was 95.73 and 65.79 kHz/% for the first resonant frequency and second resonant frequency. At a hydrogen concentration of 4%, the response time and recovery time is 85 s and 15 s, respectively. Furthermore, the thin film with a small-sized beam structure effectively improves the Q-value of the first resonant frequency of the resonator, compared with the previous trampoline structure [19]. The advantages including compact size, absence of specialized packaging requirements, and all-fiber construction make this device anticipated in extreme environment hydrogen sensing.

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Wei Ding was born in Anhui, China, in 1998. He received the B.E. degree in mechatronics and automation from Huaqiao University, Quanzhou, China, in 2020, with a major in measurement and control technology and instrument. His research interests include the design, fabrication of fiber graphene resonators and their applications.

Shen Liu was born in Henan, China, in 1986. He received the B.Eng. degree in electronic and information engineering from PLA Air Force No.1 Aviation University, Changchun, China, in 2008, the M.S. degree in circuit and system from the Chongqing University of Posts and Telecommunications, Chongqing, China, in 2013, and the Ph.D. degree in optics in Shenzhen University, Shenzhen, China, in 2017. From 2017 to 2018, he was with Aston University, Birmingham, U.K., as a Postdoctoral Fellow. Since 2018, he has been with Shenzhen University, as an Assistant Professor. He has authored or coauthored 11 patent applications and more than 30 journal and conference papers. His research interests include optical fiber sensors, WGMs resonator, and cavity optomechanics.

Peijing Chen was born in Guangdong, China, in 1997. He received the B.E. degree in applied physics and materials from Wuyi University, Nanping, China, in 2020, with a major in optoelectronic engineering, and the M.S. degree in optics from Shenzhen University, Shenzhen, China, in 2023. His research interests include the design, fabrication of fiber graphene resonators and their applications.

Bonan Liu received the master's degree from the University of New South Wales, Sydney, NSW, Australia, in 2019. He is currently working toward the Ph.D. degree with the College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen, China. His research interests include fiber-based micro cavity and tilted fiber gratings.

Hang Xiao was born in Fujian, China, in 1998. He received the B.E. degree in electronic science and technology from Minjiang University, Fuzhou, China, in 2020, with a major in optoelectronic engineering, and the M.S. degree in optics from Shenzhen University, Shenzhen, China, in 2023. His research interests include the design, fabrication of fiber graphene resonators and their applications.

Xin Ding received the Ph.D. degree from the University of Shanghai for Science and Technology, Shanghai, China. He currently conducts postdoctoral research with Shenzhen University, Shenzhen, China, with a research focus on fiber optic high-temperature pulsation pressure sensing.

Ying Wang was born in Henan, China, in 1983. He received the B.S. degree in applied physics and the Ph.D. degree in physical electronics from the Huazhong University of Science and Technology, Wuhan, China, in 2004 and 2010, respectively. From 2010 to 2011, he was with the Department of Electrical Engineering, Hong Kong Polytechnic University, Hong Kong, as a Research Associate. From 2011 to 2015, he was with the School of Science, Wuhan Institute of Technology, Wuhan, China. Since 2015, he has been with the College of Physics and Optoelectronic Engineering, Shenzhen University, as an Associate Professor. His research interests include optical fiber sensors, photonic crystal fibers and devices, and femtosecond laser micromachining.

Yiping Wang (Senior Member, IEEE) was born in Chongqing, China, in 1971. He received the B.Eng. degree in precision instrument engineering from the Xi'an Institute of Technology, Xi'an, China, in 1995, and the M.S. and Ph.D. degrees in optical engineering from Chongqing University, Chongqing, China, in 2000 and 2003, respectively. From 2003 to 2005, he was with Shanghai Jiao Tong University, Shanghai, China, as a Postdoctoral Fellow. From 2005 to 2007, he was with the Hong Kong Polytechnic University, Hong Kong, as a Postdoctoral Fellow. From 2007 to 2009, he was with the Institute of Photonic Technology, Jena, Germany, as a Humboldt Research Fellow. From 2009 to 2011, he was with Optoelectronics Research Centre, University of Southampton, Southampton, U.K., as a Marie Curie Fellow. Since 2012, he has been with Shenzhen University, Shenzhen, China, as a Distinguished Professor. He has authored or coauthored one book, 21 patent applications, and more than 240 journal and conference papers. His research interests include optical fiber sensors, fiber gratings, and photonic crystal fibers, optical fiber sensors, fiber gratings, and photonic crystal fibers. Prof. Wang is a Senior Member of the Optical Society of America and the Chinese Optical Society.