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In situ determination of the complex permittivity of ultrathin H₂-infused palladium coatings for plasmonic fiber optic sensors in the near infrared

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The high price and volatile supply source of oil as well as the desire to move towards greener sources of energy have created a growing interest in the use of alternative fuels, such as hydrogen. It is vital to have an inexpensive device that can quickly, sensitively, reliably and safely monitor hydrogen concentrations in case there is a leak. In this paper, we report measurements of the complex permittivity of 7 nm thick palladium thin films exposed to concentrations of 0 to 3% (by volume) hydrogen in nitrogen at wavelengths near 1310 nm. Measurements were carried out with a tilted fiber Bragg grating first coated with 30 nm of gold and then palladium at several thicknesses between 3 and 43 nm. The tilt angle of the grating was fixed at 23 degrees in order to allow the excitation of surface plasmon resonances on the gold surface by high order cladding modes in air at wavelengths near 1310 nm. Simulations of the grating response based on measurable experimental parameters indicate that for palladium thicknesses between 3 and 10 nm, the measured changes in the grating transmission become independent of thickness. Therefore, for a 7 nm thick film, any change in transmission can be traced directly to changes in permittivity. The relative change of the permittivity of the palladium layer was found to scale linearly with hydrogen concentration with a scaling factor of $-0.15/\%H_2$ for hydrogen concentrations between 0 and 1.7%. The limit of detection of the grating configuration used was determined to be 380 ppm at three times the standard deviation for measurements averaged over 80 seconds. Using standard fiber optic instrumentation and a single mode fiber, the signal to noise ratio was over 100.

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1 Introduction¹

Hydrogen (H₂) is a promising energy source and a perfect candidate to help supply the energy demands of the world while reducing toxic emissions from fossil fuels.¹ However, hydrogen is also a highly flammable and explosive gas at concentrations ranging from 4–75% in air, with a low ignition energy and high heat of combustion.² The increase in its industrial use as a clean energy source^{3,4} has precipitated the need for safe, sensitive, robust, real-time, remote, compact and cost-effective sensors to monitor hydrogen concentrations.⁵

Many high performance hydrogen sensors have been reported in recent years,⁶ among which optical fiber sensors have outstanding advantages, such as intrinsic safety, corrosion resistance, suitability for remote sensing, and immunity to electromagnetic interference.⁷ Optical fiber hydrogen sensors usually rely on sensitive and specific reactive thin film coatings to translate hydrogen concentrations into optical signals: in particular, palladium (Pd) metal has been a favorite coating as it absorbs hydrogen in proportion to its relative concentration thereby forming either palladium hydride (PdH_x, where *x* is the atomic ratio of H: Pd) or a mixture of molecular hydrogen in Pd. This chemical change is associated with volume changes as well as modifications to the real and imaginary parts of the metal permittivity.^{8,9} Many Pd-coated optical fiber hydrogen sensors based on fiber Bragg gratings,^{10–13} micro fibers,^{14,15} etched fibers¹⁶ and photonic crystal fibers¹⁷ have been demonstrated or theoretically proposed. The present paper aims at determining the optical properties of ultrathin (less than 10 nm) films of Pd exposed to H₂ concentrations between 0 and 3% (by volume), using a recently developed gas-phase fiber optic surface plasmon resonance (SPR) sensor.¹⁸

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Fiber SPR sensors form a subset of optical fiber sensors that benefit from the high confinement of intense electromagnetic fields at the surface of the metal layers deposited on the fiber.^{19–22} Such sensors have been predominantly used in biochemical sensing where the surface sensitivity is a great advantage and where the phase matching of the surface plasmons to propagating fiber modes is facilitated by the fact that the surrounding medium is a liquid with a refractive index relatively close to that of the fiber.²¹ Even though Pd is a metal and should be useable for SPR, few such H₂ sensors, and especially fiber-based sensors, have been reported so far. The reason for this is that the propagation constant of surface plasmons at the metal–air interface is strongly mismatched to that of light guided in the fiber, which makes the coupling of light to the SPR difficult, but also because in order to have the best (narrow and high attenuation) possible SPR, the thickness of the metal must be at least several tens of nm, which slows the response time of the Pd to H₂ in-diffusion. The coupling problem has so far only been demonstrated for bulk SPR sensors using a Pd-coated glass prism based on the Kretschmann configuration and a very low value of the incidence angle,²³ and for a fiber with a single Pd layer deposited onto an unclad fiber where the use of strongly off-axis input light launching in the fiber allowed the excitation of the SPR.²⁴

In order to facilitate coupling to surface plasmons in air, several multi-layered SPR hydrogen sensors have been proposed in recent years. The use of an SPR active metal such as Au or Ag coupled with a high refractive index insulator or semiconductor film, such as Si or Ta₂O₅, and finally the H₂-active Pd layer has allowed the formation of plasmon-assisted resonance at more accessible propagation constants in air.^{25–28} Finally, another technique to couple fiber modes to a single metal layer SPR in air through the use of a customized tilted fiber Bragg grating (TFBG) was demonstrated in 2016 by our group to have an experimental limit of detection of the order of 10 ppb (for oscillating refractive index changes).¹⁸ This new sensor is configured here for its first application in specific chemical gaseous sensing and it is used to measure the complex permittivity of PdH_x as a function of H₂ concentration. The first step of the process is a combination of simulations and experiments on the effect of Pd thickness on the response of TFBG-SPR sensors, since this parameter impacts the response speed and reversibility.²⁹ Once the optimum thickness is chosen, further simulations are used to correlate the experimentally measured changes in the sensor response upon exposure to various concentrations of H₂ with changes in the optical properties of PdH_x. The determination of the effect of H₂ on Pd can then be used to predict the performance of other similar sensor devices without having to calibrate each sensor individually. Of particular interest is the fact that for TFBG-SPR sensors with 30 nm thick gold coatings operating at wavelengths near 1.3 μm, the response of the sensor becomes insensitive to small changes in Pd thickness when this thickness is between 3 and 10 nm, thereby isolating the effect of H₂ adsorption to permittivity changes only, which leads to a great simplification of the data analysis. It is important to note that because of the additional

layer of Pd and operation at wavelengths near 1300 nm, a 30 nm gold thickness is used here instead of 50 nm, which is the preferred thickness for the SPR sensor in liquid media at wavelengths near 1550 nm.³⁰ The paper is organized as follows: in Section 2, we briefly describe the sensor principle and the influence of the Pd thickness on the SPR response, from which an optimum Pd thickness of 7 nm is determined. Section 3 then presents the experimental results and simulation support for the relationship between the complex permittivity of PdH_x and hydrogen concentration in the range from 0 to 3% (*i.e.* up to just below the flammability threshold of H₂). This important result supports and confirms the fact that there is a linear relationship between concentration and complex permittivity, furthermore that the real and imaginary parts of the permittivity scale by the same amount and finally that the value we obtain for the scaling factor conforms to previous partial findings at similar concentrations. The detection limit based on the relatively high signal to noise ratio of the TFBG-SPR device, the sensitivity and the standard deviation of the measurements are also reported. Section 4 summarizes and concludes our results with a discussion of their impact.

2 Methods, simulations and optimization

2.1 Simulations

Unlike standard fiber Bragg gratings, the response of TFBGs depends on the state of polarization of the input light launched in the core because the tilt in the grating planes effectively breaks the cylindrical symmetry of the fiber. In particular, when the input core light is *p*-polarized relative to the inclination plane of the grating fringes, high order cladding modes (with low values of effective indices) have electric fields polarized radially at the cladding surface, *i.e.* the equivalent of TM polarization in the planar case and thus ideally polarized to excite surface plasmons on metal coatings. The consequence for the grating transmission is a relatively narrow spectral region where the amplitudes of the cladding mode resonances are strongly diminished because of the coupling to a surface plasmon.^{31,32} For the results to be reported here, the fiber used was a boron germanium co-doped highly photosensitive single-mode fiber (FIBERCORE PS1250/1500), and the gold coated TFBGs were fabricated as reported in ref. 22 with a Bragg wavelength of 1543.34 nm for the core mode back reflection. This fiber has been designed to match the mode field diameter characteristics of a typical, dual-wavelength, 1310 nm and 1550 nm telecommunications fiber, and it remains single-mode at wavelengths near 1300 nm where the SPR effects occur in our sensors when the gold coating is exposed to air or dilute gases.

Fig. 1 shows a typical experimental transmission spectrum of an 18 mm long, 23 degree tilt TFBG (internal angle relative to the fiber cross section) coated with 30 nm of gold and measured in air with input light *p*-polarized. The fine comb of cladding mode resonances is more complex than that of TFBGs with smaller tilt angles but a clear SPR signature is observed near 1312 nm.

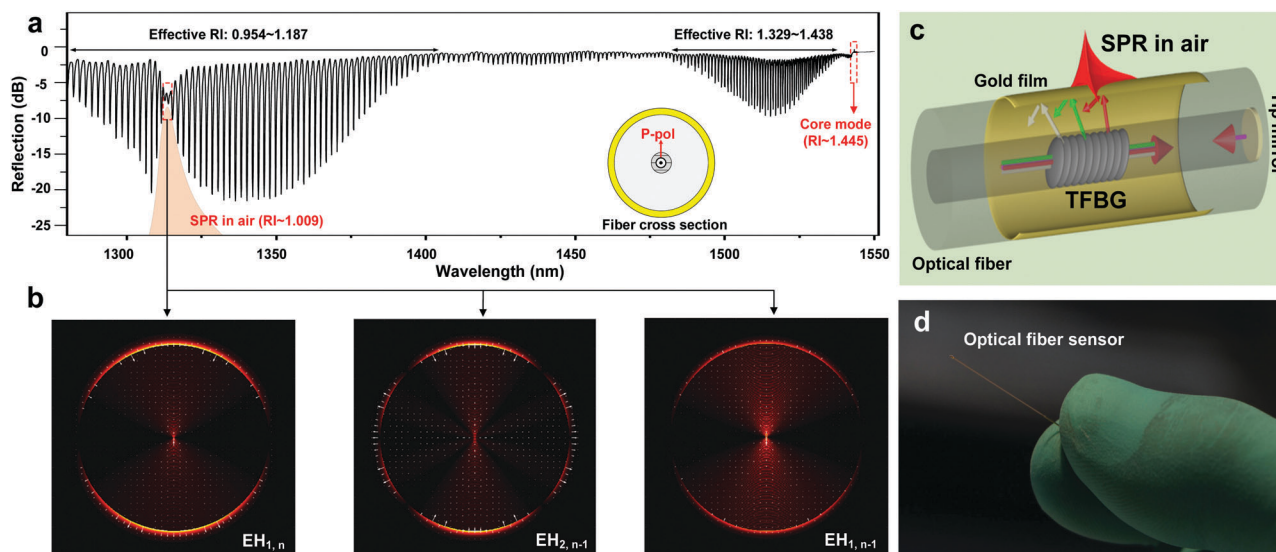


Fig. 1 (a) Experimental transmission spectrum in air for a 23° tilt TFBG in a standard single mode optical fiber with 30 nm of gold deposited on the cladding surface and the input light polarized linearly along the vertical axis, *i.e.* *p*-polarized relative to the tilt direction (see inset for orientations). (b) Simulated electric field intensity distributions of three hybrid plasmonic cladding modes located within the SPR bandwidth. These modes have effective indices near 1.0 and between 5 and 30% of their total power propagating within a 2 μm thick layer above the gold surface. (c) Reflective TFBG-SPR sensing system.²² a tilted grating is inscribed in the core of a standard single mode fiber by exposure to intense ultraviolet irradiation through a phase mask; a thin metal coating is deposited on the fiber cladding and an additional gold coating (or broadband chirped fiber Bragg grating) is added downstream of the TFBG to reflect the whole incident spectrum through the grating and towards the interrogation system. For a given grating period and light wavelength, the cladding modes coupled from the core by the grating will be phase matched with surface plasmons propagating along the outside metal surface. (d) Photograph of the configuration for the gold-coated fiber-optic sensing probe.

In fact, the tilt angle was chosen so that strong coupling occurs to high order cladding modes with the real part of their effective index close to 1.01, *i.e.* synchronous with the effective index of the surface plasmon of a gold surface in air at these wavelengths.

The simulation of the device transmission spectrum was carried out first by solving for the modes of the fiber structure (inclusive of core, cladding, metal layers, and outside medium) with a complex vectorial finite-difference algorithm, and then using coupled mode theory as described in ref. 33 for the transmission of TFBGs. The simulation parameters were a core radius of 4.1 μm with a refractive index of 1.4545, and a cladding

radius of 62.5 μm with a refractive index of 1.4467. The gold coating had a thickness of 30 nm and a complex refractive index of 0.4538–8.37082i while the Pd layer had an index of 2.7423–7.3407i (please note the values of refractive index of all solutions and optical fiber materials (core and cladding) were referenced to 1320 nm³⁴) and several values of thickness. These simulations first confirm that the real part of the surface plasmon effective index observed experimentally is near 1.009. Fig. 2 shows the simulated effective indices of the modes most strongly coupled to the surface plasmon, as indicated by the fact that they have the largest imaginary parts: they are the TM_{0m} ,

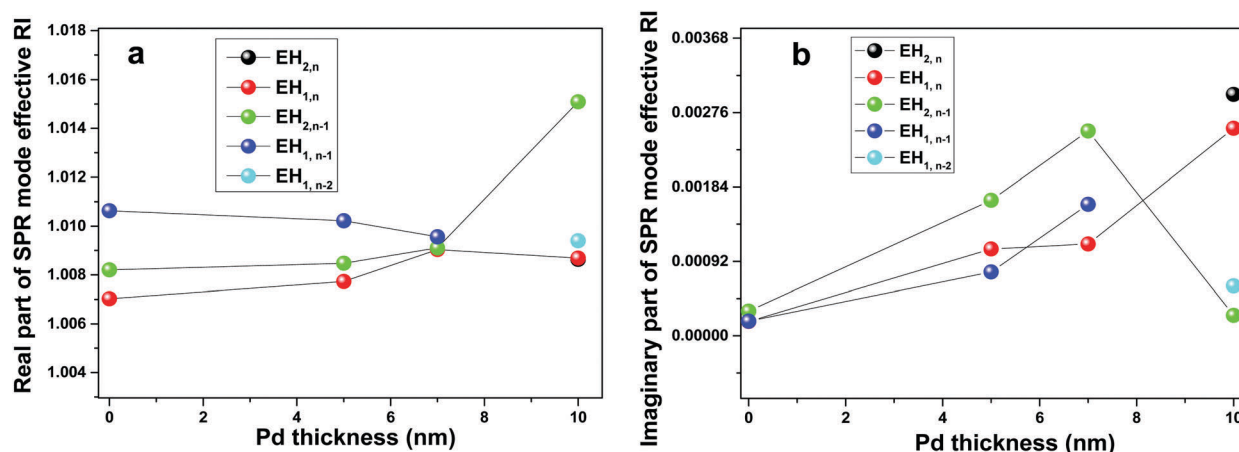


Fig. 2 Simulated real part (a) and imaginary part (b) of the effective indices of cladding modes that are phase-matched to the surface plasmon over the metal surface in the air.

Table 1 Performance comparison of (long range) SPR-based hydrogen sensors

Sensing platform	Sensitive film and thickness	Concentration range	Limit of detection (year)	Ref.
Step-index MMF without cladding	35 nm Au/180 nm SiO ₂ /3.75 nm Pd	0.5–4%	0.5% (2013)	27
Hetero-core structured SMF	25 nm Au/60 nm Ti ₂ O ₅ /5 nm Pd	0–4%	— (2013)	28
Cytop membrane waveguide (LRSPR)	5 nm Pd	0–3%	870 ppm (2016)	37
TFBG (LRSPR)	30 nm Au/7 nm Pd	0–1.7%	380 ppm (2018)	This work

EH_{1n} and EH_{2n} modes and they have a radial order n greater than 160. Table 1 shows that without Pd, the imaginary parts of these modes vary from ≈ 1.8 to 3×10^{-4} and that addition of a Pd layer up to 7 nm thick increases the imaginary part by as much as 7 times. Fig. 1b further shows the distribution of the mode field power density (*i.e.* the Poynting vector) over the cross-section of the gold coated fiber for some SPR-active modes, with the high field power located just above the cladding surface. As will be shown below, the EH_{1n} mode most strongly coupled to the SPR has a surface power fraction near 47% and hence should be the most sensitive. However, this mode is also so attenuated and weakly coupled to the incident core mode that it actually disappears from the transmission spectrum and is impossible to monitor. The next mode on the short wavelength side is the TM_{0n} mode, which has a smaller attenuation and still 11% of power propagating above the fiber surface, and it is the one that will be used for measurement purposes.

In order to facilitate the use of the TFBG as a measurement tool, the schematic and actual device configuration chosen are shown in Fig. 1c and d. The metal coated TFBG is cut and the fiber end coated with a thin layer of gold acting as a broadband mirror. Light from a broadband source is coupled into the fiber through a coupler or circulator such that the reflected signal from the end mirror can be extracted and measured. This allows the measurement of the TFBG transmission spectra in reflection so that the device can be inserted into any location where the H₂ concentration needs to be monitored. In this configuration, the input light goes through the TFBG twice, an effect that is taken into account in the simulations of the spectra.

2.2 Optimization of palladium thickness

In this section, the simulation tool is first used to find the parameters of the gold coated TFBG used in the experiments

from the measured spectrum. Apart from the known parameters of the Corning SMF-28 fiber used, the length of the grating and internal tilt angle, the remaining unknowns, which are the effective period and index modulation amplitude of the grating, can be found from the Bragg wavelength of the grating and the peak-to-peak amplitude of any given resonance.³³ For one of the devices used in the experiments, the measured spectrum shown in Fig. 3a was modeled with a refractive index modulation amplitude of 0.0012 and a period along the fiber axis of 532.73 nm.

While the simulated spectrum shown in Fig. 3b does not fully match the experimental one, the main features are preserved and the grating parameters were adjusted so that the position, shape and peak-to-peak amplitude of the resonance located just on the blue side of the SPR maximum are identical to the measured one. This resonance provides a good compromise between plasmonic sensitivity enhancement and quality factor (narrow linewidth and large amplitude).²² With the model fiber thus obtained, simulations of the effect of increasing Pd thickness can be carried out and compared to the spectrum of this resonance measured after different durations of Pd deposition (Fig. 4).

The main outcomes of this analysis are that the identified resonance red-shifts rapidly with increasing Pd thickness and that its amplitude first decreases and then increases again, both in experiments and simulations. These changes appear to saturate for thicknesses exceeding 50 nm, indicating that the combined metal layers become thicker than the field penetration, as can be expected. Of particular interest is the fact that for thicknesses between approximately 3 and 10 nm, the amplitude of the simulated resonance becomes quite insensitive to thickness changes while the wavelength shifts rapidly. In spite of the

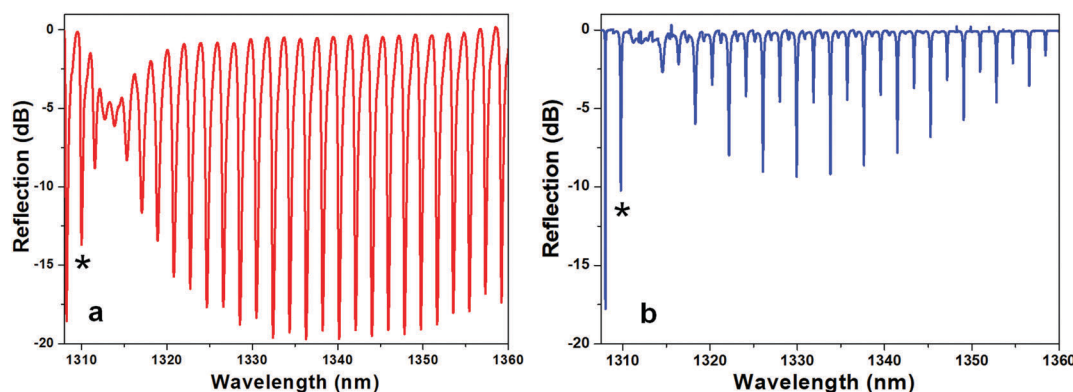


Fig. 3 Measured (a) and simulated (b) spectrum (zoomed SPR wavelength range) of an 18 mm long TFBG with a 30 nm thick gold coating and an internal tilt angle of 23°. The refractive index modulation amplitude for which the simulated amplitude of the near 1310 nm resonance is equal to the measured one is 0.0012.

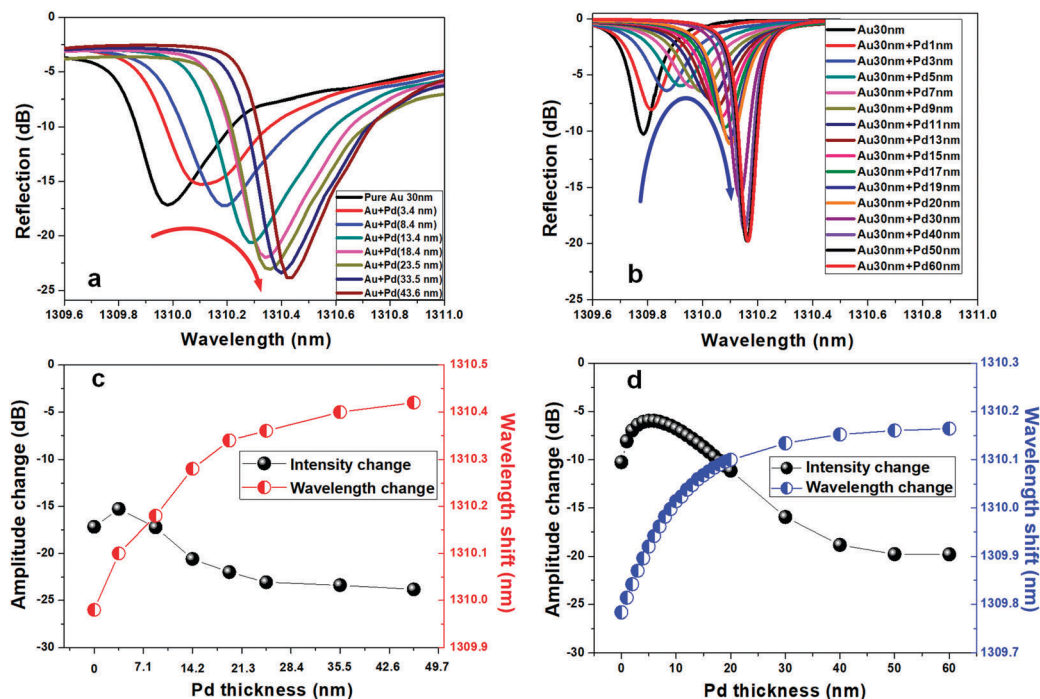


Fig. 4 Experimental (a and c) and simulated (b and d) SPR spectral response when adding Pd to the gold coated TFBG (monitoring the 1310 nm mode resonance marked with “*” in Fig. 3): (a) and (b) show how the selected mode resonance shifts in the spectrum with increasing thickness of Pd; (c) wavelength and peak-to-peak amplitude change of the 1310 nm resonance as a function of deposition time and (d) the simulated Pd film thickness.

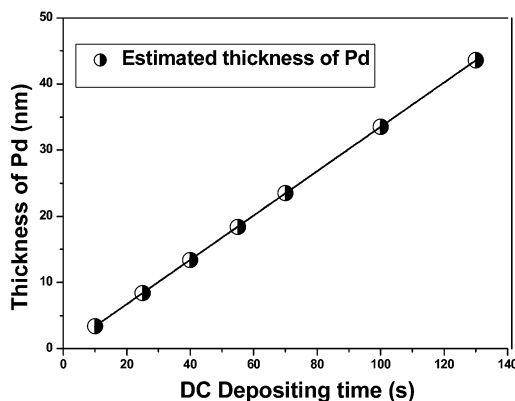


Fig. 5 Estimation of the thickness of Pd with different depositing times according to SEM when we deposited Pd for 20 s under the same conditions.

lack of data for very small thicknesses, the experimental spectra show a similar effect with a maximum for a Pd deposition time of 10 seconds that corresponds to a thickness of 3.4 nm (from Fig. 5). This is interesting in the sense that the reaction of Pd with H_2 leads to volume changes in addition to chemical changes,⁹ so if we use a thickness in the aforementioned range, the optical response that is measured by the TFBG will only be impacted by the chemical change (*i.e.* the change in permittivity) and not by thickness changes. Therefore, further simulations were carried out to determine the effect of the Pd permittivity on the wavelength and amplitude of the 1310 nm resonance for several thicknesses between 0 and 20 nm and a 35% change in

complex permittivity. One important assumption made in this simulation is that the real and imaginary parts of the complex permittivity change at the same rate, *i.e.* $\epsilon(PdH_x) = h(c) \cdot \epsilon(Pd)$, where $h(c)$ is a factor depending on the H_2 concentration, as indicated in ref. 24. Early reports have demonstrated that the parameter $h(c)$ is a nonlinear function decreasing with hydrogen concentration c and taking values less than 1. This function is an empirical one, the values of which can only be determined by comparison between simulation and experiment, which will be the case in the following.

The results of this analysis show in Fig. 6 that for a given thickness, the resonance wavelength does not change but the amplitude increases with decreasing refractive index. Converting the dB scale of the reflection measurement in linear units, the sensitivity, *i.e.* the rate of change of the reflected minimum power relative to its value for pure Pd ($h = 1$), *i.e.* $RP = P(h)/P(1)$, increases with thickness from 1.1 per fractional change in permittivity (Δh) at 2 nm, to $1.62 \Delta h^{-1}$ at 7 nm and more slowly to $1.83 \Delta h^{-1}$ and $1.91 \Delta h^{-1}$ at 12 and 20 nm, respectively. While it is customary to seek the highest sensitivity in such experiments, here, other factors come into play, namely the response time (faster for thinner Pd films) and the desired reversibility of the Pd- H_2 reaction. Because of this, a thickness of 7 nm was chosen for experiments designed to determine the permittivity of PdH_x with sufficient precision to allow the further use of such devices for H_2 sensing in practical applications.

2.3 Hydrogen reactions with Pd-coated, Au-coated TFBG

Fig. 7 shows the experimental setup for the measurement of the complex refractive index of thin Pd films exposed to various

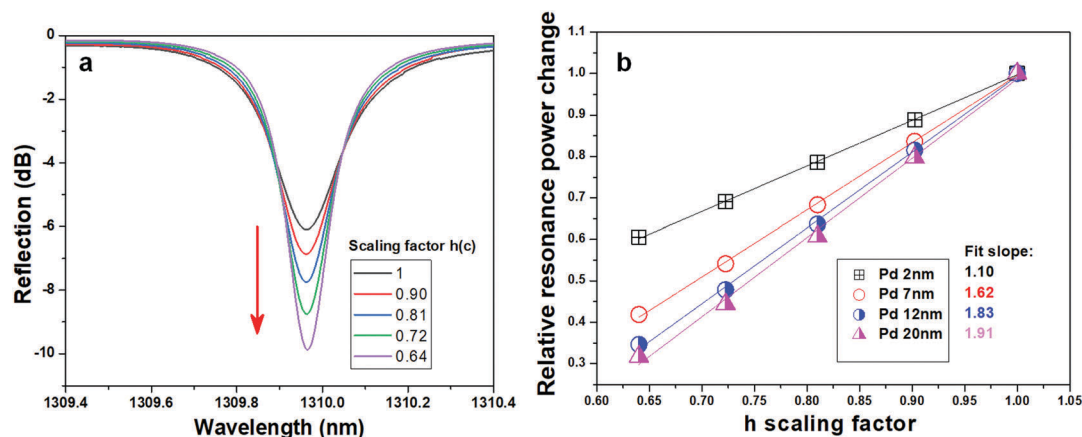


Fig. 6 (a) Typical simulated response of the 1310 nm resonance to changes in the complex permittivity of a 7 nm thick Pd film on top of the 30 nm thick gold coating; (b) peak-to-peak amplitude of the 1310 nm resonance as a function of the fractional change in refractive index for 4 values of Pd thickness.

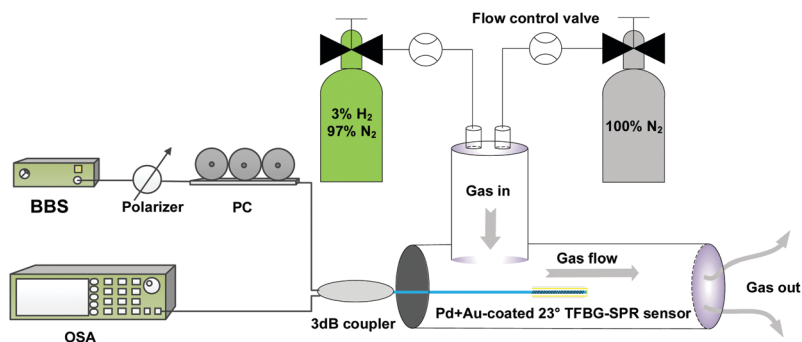


Fig. 7 The experimental setup to measure the coated TFBG response to various concentrations of H₂.

concentrations of H₂ based on a Au-Pd coated 23° TFBG with an ~ 200 nm thick gold mirror deposited on the cleaved end by direct current (DC) magnetron sputtering followed by a protective layer of 500 nm of SiO₂ using radio-frequency (RF) sputtering. The Pd coatings used were also deposited by magnetron sputtering. Light was launched in the core of the plasmonic TFBG from a broadband source (BBS) with a wavelength range of 1280–1560 nm and the reflection spectrum was monitored by an optical spectrum analyzer (OSA) with a wavelength resolution of 0.02 nm. A linear polarizer and a polarization controller (PC) were placed upstream of the coupler to adjust and orient the state of polarization of light so as to provide the strongest SPR excitation. At this measurement resolution, spectra could be recorded continuously every 10 seconds. The gas chamber was made of a section of plastic tube that had an inlet and an outlet to allow the H₂-N₂ mixture to flow in and out. The flow rates of hydrogen and nitrogen gases were individually controlled: the flow rate of nitrogen was kept at 500 cubic centimeters per minute (ccm) while the flow rate from the 3% hydrogen in nitrogen cylinder was adjusted according to the required concentration. The inset of Fig. 7 shows the configuration of the Au-Pd coated TFBG probe. The azimuthal uniformity of the film thickness over the fiber surface was achieved by rotating the fiber around its axis during all depositions except for the end-face mirror. The deposited gold film thickness was

measured to be 32 nm and a further deposition of Pd for 20 seconds yielded an additional thickness of ~ 7 nm (from interpolation of the results in Fig. 5). Cross-sections of TFBGs with gold only and with gold-palladium combined films are shown in Fig. 8a and b along with the corresponding spectra. Perfect thickness uniformity around the fiber circumference is not absolutely necessary to observe SPR effects (much of our earlier papers on this topic, available in the reference list, were obtained with double sided depositions that were much less uniform than those used here). The current method does provide very uniform coatings, as shown in ref. 35. Fig. 8c shows that the gold film has a RMS roughness of 0.7 nm. This roughness impacts the SPR response and this is the cause of the difference between the envelopes of the measured and simulated spectra (Fig. 3 and 4) since the simulated spectra assume “perfect” films with no additional loss from scattering. (Scattering adds a broadband additional loss in spectra, with some widening of the resonances.) This being said, when fitting a single resonance (Fig. 4a and b), the fact that we adjust the grating strength in the simulation to fit the measured resonance amplitude takes any scattering effect on the resonance into account implicitly. Further changes in scattering arising from adding up to 7 nm of Pd are negligible, as can be seen in Fig. 8 by looking at resonances away from the SPR, and so are those following H₂ incorporation into the Pd. Therefore,

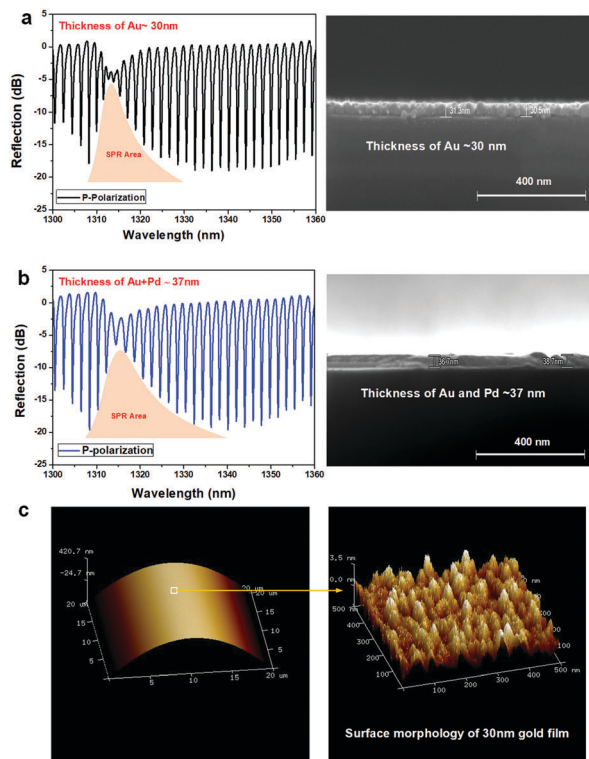


Fig. 8 (a) Reflection spectrum of a 30 nm-Au coated TFBG and scanning electron micrograph of a cross-section of the gold film at the fiber surface; (b) same as (a) but for the TFBG with an additional 7 nm thick layer of Pd. The SPR attenuation spectrum is shown as the shaded area in both spectra; (c) AFM of 30 nm gold film over the optical fiber (fabricated by magnetron sputtering).

and this is a key point of this whole work, we believe that our model reflects the experimental situation accurately, for a single resonance located on the shoulder of the SPR envelope.

3. Results and discussion

Fig. 9(a) shows the simulated distribution of the Poynting vector magnitude of the radially polarized electric field of the 1312 nm mode resonance near the cladding surface boundary: a strong enhancement of the mode power just above the metal layer is clearly seen due to coupling to the surface plasmon. Perturbations of any of the layer permittivities, such as those arising from the chemical reaction between H_2 and Pd, will be felt by the mode field and result in changes of its propagating characteristics and hence of the TFBG transmission spectrum. Such changes are clearly seen in Fig. 9(b), where the measured amplitude of the 1312 nm resonance is seen to increase when the ambient medium changes from pure N_2 to 3% H_2 in N_2 . It is interesting to note that the wavelength does not appear to change and this is confirmed by the more detailed experiment shown in Fig. 9c and d. This means that either the thickness does not change (unlikely) or that as shown by the simulations in Section 2, the response of the TFBG is indeed insensitive to small thickness changes when its initial thickness is near 7 nm.

The relative power change of the 1312 nm resonance is linear over the concentration range from 0 to 1.7% with a slope of $\Delta RP/\Delta c\% = -0.15$ while the wavelength remains constant at $1312.206 \text{ nm} \pm 0.001 \text{ nm}$ (Fig. 9c and d). Comparing these results to the simulations carried out for the TFBG with a 30 nm gold coating and a 7 nm thick Pd film ($\Delta RP/\Delta h = 1.62$) allows the determination of the complex permittivity of PdH_x ($\epsilon_c(PdH_x) = h(c\%) \cdot \epsilon_c(Pd)$), where $h(c\%) = 1 + (\Delta h/\Delta c\%) \cdot c$ as follows:

$$\Delta h/\Delta c = (\Delta RP/\Delta c\%)/(\Delta RP/\Delta h) = -0.093$$

(for $c\%(H_2)$ between 0 and 1.7%) (1)

This result is consistent with the literature since for a concentration of 1.7%, the value of h is equal to 0.84, within the range reported previously (between 0.75 and 0.9), and this supports the broadly used observation that the real and imaginary parts of the complex permittivity of PdH_x scale by the same amount as a function of H_2 concentration.^{19,36,37} Higher concentrations of H_2 do not cause further increases in the resonance amplitude for this particular configuration and hence cannot be measured, but the current approach does yield important information at concentrations covering about half the range over which the H_2 mixture is not igniting easily. At room temperature, the 1–2% concentration range also corresponds to the beginning of the transition of the PdH_x compound from the so-called alpha to the beta phase, where the alpha phase corresponds to a state where the H_2 is just dissolved into the Pd matrix and not chemically bonded to it whereas the beta phase corresponds to chemically stable palladium hydride.

In practice, once a device is fabricated (TFBG + gold + Pd), it is measured in air (known to be free of H_2) to obtain a starting spectrum (as in Fig. 3). Then, inverse modelling is used to fit the only adjustable parameter that may vary from device to device, *i.e.* the initial amplitude of the SPR resonance of that particular device. After the fit, the model reproduces the initial state of the SPR resonance (Fig. 4). Finally the response of this particular device to H_2 exposure can be predicted using the found relationship (eqn (1)) between the H_2 concentration and complex permittivity of Pd. Therefore, each device does not need to be exposed to different concentrations of H_2 prior to use to establish its calibration, which would be prohibitively expensive.

Another design criterion that resulted in giving up some sensitivity by going with a thinner Pd layer was the re-usability of the sensor and its temporal response. Fig. 10 shows a cycling experiment where the H_2 concentration was suddenly changed from 0 to 3%. The initial response is 100 s while the recovery takes approximately 400 s. These results are comparable to those of ref. 37 (response and recovery times of ~ 50 s, for a Pd thickness of 5 nm on a gold waveguiding membrane of 20 nm thickness). That configuration had a sensitivity magnitude, measured for small H_2 concentrations, of the order of $0.3 \text{ dB}/c\%(H_2)$, *i.e.* similar to the one measured here ($-0.79 \text{ dB}/c\%(H_2)$ after converting units). Finally, a closer examination of the initial plateau in Fig. 10a (shown as Fig. 10b) shows that the standard deviation (measurement noise) of the resonance amplitude for a

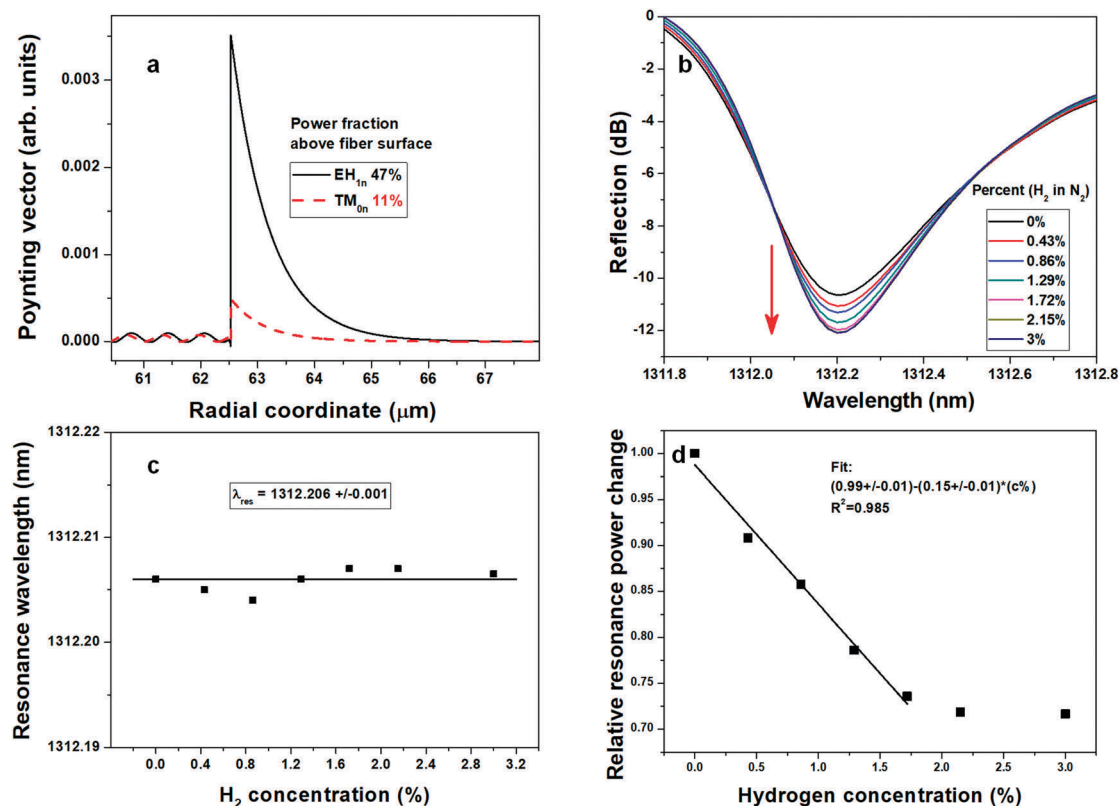


Fig. 9 (a) Magnitude of the Poynting vector for the radially polarized SPR-cladding mode near the cladding surrounding boundary. (b) Measured reflected spectrum near the 1312 nm resonance as a function of H_2 concentration. (c) Measured wavelength and (d) peak-to-peak amplitude change of the 1312 nm resonance as a function of H_2 concentration.

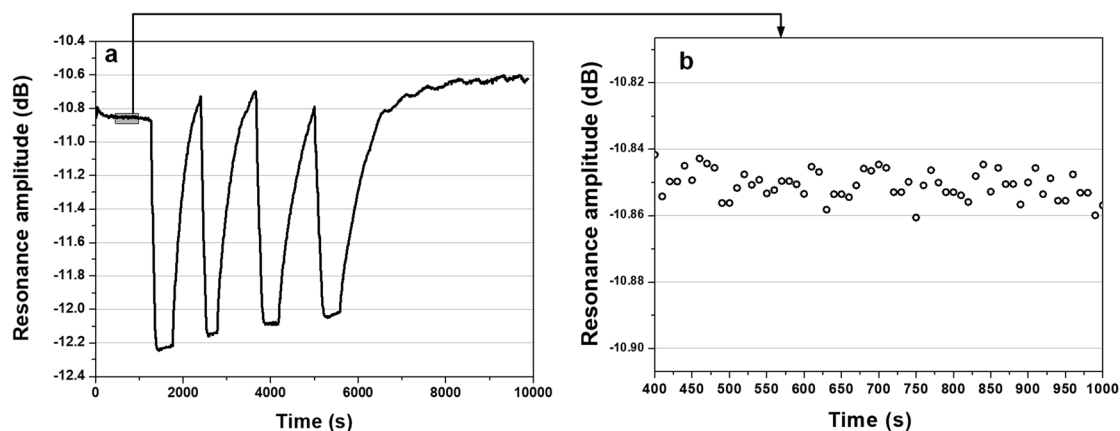


Fig. 10 (a) Response of the 1312 nm resonance amplitude to successive exposure of the device to alternating concentrations of 0 and 3% H_2 . (b) Zoom on the response between 400 and 1000 s showing the response noise.

constant (0%) H_2 concentration is ± 0.01 dB. Therefore, the limit of detection can be estimated in the usual manner by a measurement value equal to three times the standard deviation, which corresponds to a concentration of 0.038% or 380 ppm. Again, this is to be compared with ref. 37, where a detection limit of 290 ppm was estimated from a linear approximation to their nonlinear response curve over one measurement point at 0.6% H_2 (this value was based on a signal to noise ratio of 1 at the detection limit. With the more widely accepted ratio of 3,

which we used, the detection limit in ref. 37 is 870 ppm). The sensing performances and structures of various types of (long range) SPR-based hydrogen sensors mentioned above are presented in Table 1. In terms of the signal to noise ratio, the power oscillations in Fig. 10a are more than 100 times larger than the noise seen in Fig. 10b. Finally, it is clear that the performance of this device drifts with successive cycling, which is a common feature for Pd coated sensing devices and is due to irreversible changes in the structure of the coatings, as described

often (and in particular in ref. 9). Therefore in its current state, the devices described here will perform best as part of alarm systems to detect when the concentration of H₂ exceeds predetermined levels. After an alarm, the device should be replaced.

4. Conclusion

The complex permittivity of a nanoscale layer of Pd exposed to H₂ volume fractions between 0 and 1.7% in N₂ was determined at wavelengths near 1310 nm using a plasmon-assisted measurement by a tilted fiber Bragg grating (the sensor still responds to concentrations up to 3% hydrogen, but nonlinearly and it gradually saturates beyond 1.7%). The complex permittivity decreases linearly by a factor equal to 0.076 per %-change in H₂ concentration in the range from 0 to 1.7%. Simulations and measurements indicate that the optical properties of the fiber grating coated with 30 nm of gold and 7 nm of palladium can be modelled with a combination of a finite difference complex mode solver and standard coupled mode theory. These simulations also indicate that the grating response is insensitive to thickness changes when the thickness of the Pd film lies in the 3–10 nm range. Therefore, knowledge of the complex permittivity of Pd as a function of H₂ concentration can be used to develop other sensors based on coated optical fibers and also to avoid having to calibrate individual sensors prior to use: a simple measurement in air enables the extraction of all the relevant parameters that can then be used to extract H₂ concentrations from changes in the sensor response. This “model-based” calibration of each sensor from a simple initial measurement in air is the key point that will enable the mass production of low cost, disposable sensor devices fabricated using mass production techniques already developed for FBGs in telecommunications and physical sensing (for strain and temperature). The response time of the device was measured to be of the order of 100 s and the recovery was 400 s, over several cycles between 0 and 3% H₂. While there is a small drift in response over successive cycles of exposure to H₂, the low cost of the sensor transducer enables its use as a single use disposable device in alarm systems for H₂ leaks approaching flammability concentrations. Finally, the limit of detection for H₂ concentrations below 1.7% was determined from the measured noise and detection sensitivity to be 0.04% at a level equal to 3 times the noise.

Conflicts of interest

There are no conflicts to declare.

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