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Abstract

We demonstrate an optically active antireflection, light absorbing, optical coating as a hydrogen gas sensor. The optical coating consists of an ultrathin 20 nm thick palladium film on a 60 nm thick germanium layer. The ultrathin thickness of the Pd film (20 nm) mitigates mechanical deformation and leads to robust operation. The measurable quantities of the sensors are the shift in the reflection minimum and the change in the full width at half maximum of the reflection spectrum as a function of hydrogen gas concentration. At a hydrogen gas concentration of 4%, the reflection minimum shifted by ~46 nm and the FWHM increased by ~228 nm. The sensor showed excellent sensitivity demonstrating a 6.5 nm wavelength shift for 0.7% hydrogen concentration, which is a significant improvement over other nanophotonic hydrogen sensing methods. Although the sensor's response showed hysteresis after cycling hydrogen exposure, the sensor is robust and showed no deterioration in its optical response after hydrogen deintercalation.

Keywords: Anti-reflection coatings, Hydrogen sensing, Light absorbers, Thin-films.

1- Introduction

Optical coatings are present in almost every optical instrument, with widespread applications ranging in displays and lighting [1,2], to anticounterfeiting [3], and photovoltaics [4]. Recently, absorptive, anti-reflection optical coatings were developed where either transmission is not of importance, e.g., structural coloring [5], and realization of generalized Brewster angle effect [6], or where high absorption is desired, e.g., for heat-assisted magnetic recording [7], solar-thermal power generation [8], and radiative cooling [9].

Light absorption is realized in optical coatings when light is critically coupled to the resonator, i.e., the absorption rate is equal to the reflection and transmission rates. This occurs when the interfering waves are out of phase (phase condition), and the out-of-phase waves are of equal amplitude (amplitude condition) [10,11]. For ultrathin film optical coatings light absorbers, critical light coupling is typically achieved by two strategies; (1) using a lossy-dielectric on a highly reflective substrate [12], e.g., Ag, Au, or Al, or (2) using a lossless dielectric on a low-reflectance substrate [13], e.g., Ni, Ti, or Pd. In addition, it has been shown that dielectrics with high refractive index lead to angle independent light absorption [11]. Angle independent light absorption leads to robust operation of optical coatings even on rough surfaces such as unpolished glass or paper [14].

On the other hand, hydrogen sensing is of crucial importance to industries where hydrogen gas (H_2) is present, e.g., in nuclear power stations, coal mines, lighting industry, and semiconductor manufacturing, etc., [11]. Hydrogen is flammable with low ignition energy at concentrations from 4% to 75% [15]. Hydrogen sensors must be able to provide strong response to concentrations significantly lower than the explosive level of 4% to provide adequate warning before an explosion hazard takes place [16]. Although there exist many well-established hydrogen sensing technologies by measuring, e.g., the change in resistance of Pd wires [17], photonic-based hydrogen sensing is especially attractive as it allows for remote optical interrogation where the raw signal is optical instead of electrical. Photonic hydrogen sensors avoid the risk of being a possible source of ignition if a hydrogen leaks occurs [18].

Several systems have been reported as a platform for optical hydrogen sensing [15,19]. In general, photonic-based hydrogen sensors measure changes in the refractive index of

materials that form hydrides , i.e., they are hydride-based refractometers [20], most commonly using palladium (Pd). When Pd is exposed to H_2, it forms palladium hydride, PdH_x, which has a different complex refractive index than Pd that depends on the hydrogen stoichiometry [21]. At low H_2 concentrations, the intercalated hydrogen atoms are randomly situated inside the Pd lattice, forming a solid solution (α phase) [22]. At higher H_2 concentrations, the hydrogen atoms are ordered in the lattice forming a hydride β phase [23], which leads to an increase in the lattice parameter by ~3.5% and an expansion of the Pd film. The resulting tensile stress causes mechanical deformation and the formation of cracks can significantly degrade sensor performance over time [16]. The formation of hydrides leads to a decrease in the absolute value of both the real and imaginary components of the complex refractive index of Pd [15]. Changes in Pd dielectric constant can be measured by directly measuring small changes in reflection [6], or scattering of Pd nanoparticles [24]. In addition, formation of hydrides can be measured indirectly by coating Pd on an optical fiber and measuring the changes in the output signal [25] or measuring the scattering of a plasmonic nanoparticle that acts as a refractometer [26]. In the context of thin Pd films, optical hydrogen sensing was demonstrated based on directly measuring changes in reflection[20] or transmission[27] due to hydride formation.

In this work, we demonstrate a nanophotonic hydrogen sensor based on an antireflective (absorptive) optical coating that suppresses light reflection in the telecommunication wavelength range. The dielectric-metal antireflective absorptive coating consists of a Ge and Pd ultrathin film. The ultrathin thickness of Pd mitigates mechanical deformation in Pd-based hydrogen sensors by reducing the clamping effect [28]. The Pd film forms a Pd hydride upon exposure to hydrogen which alters the wavelength of minimum reflection, λ_{min}, and the full width at half maximum (FWHM) of the light absorber. The measured shift in λ_{min} is ~46 nm at the critical H_2 concentration of 4%, which is significantly higher than other nanophotonic gas sensors [15,19]. Due to the high refractive index of Ge, λ_{min} is angle independent over a wide range of angles ($25^\circ - 45^\circ$), and the shift in λ_{min} is approximately the same for all the measured incident angles. We show that the change in FWHM is an important sensing parameter reaching up to $228 \pm 4nm$ at 45°. The demonstrated sensor is inexpensive and can be deposited over a large area which enables scalable hydrogen monitoring [20].

2- Experimental:

2.1- Sensor fabrication:

The sensor consists of a 20 nm thick Pd film on top of a 60 nm thick Ge layer, each deposited by electron beam evaporation at a rate of 0.5 Å. s^{-1}on a 1 mm thick glass slide (see **Fig. 1a)**. The Pd thickness was chosen to be ~20 nm to mitigate mechanical deformation by the clamping effect where the tensile stiffness of a film is inversely proportional to its thickness [15]. We chose Ge to serve as a dielectric as it has a high refractive index in the near infrared NIR region with negligible optical losses [29]. As we showed previously, a high index dielectric results in angle independent light absorption in thin-film absorbers [14]. The Ge thickness was chosen to obtain a reflection minimum within the telecom wavelength windows (~ 1300 nm-1600 nm). To expose the sensor to hydrogen, we fabricated a microfluidic channel on the sensor (see **Fig. 1a**). The channel consists of a poly (methyl methacrylate) (PMMA) body (encompassing laser micromachined inlets and outlets) and a double-sided 100-µm adhesive film defining the outlines and thickness of the microchannel. The microfluidic channel was attached to the Pd side and the reflection was interrogated from the glass side.

2.2- Experimental setup:

The sensor was placed on a variable angle ellipsometer (J. A. Woollam) to measure the angular reflectance *R* (**Fig. 1b**). To control the hydrogen concentration, a 4% hydrogen (H_2) in nitrogen (N_2) mixture was diluted by pure N_2. The ratio of the two was varied by two digital mass flow controllers (MFCs) to obtain a final concentration between 0.7 and 4%. The reflection before introducing the hydrogen was measured and recorded. It is important to note that using an ellipsometer is ideal to perform angular reflectance measurement over a wide wavelength range, however, it limits our ability to determine the exact response time of the sensor. In all cases, the response time of a hydrogen sensor depends on the hydrogen diffusion coefficient in the active material, here Pd, and the film thickness[30]. For the purpose of our experiments, we recorded the reflection after ~ 12 minutes from introducing the H_2/N_2 mixture to ensure that we observe the steady state reflection.

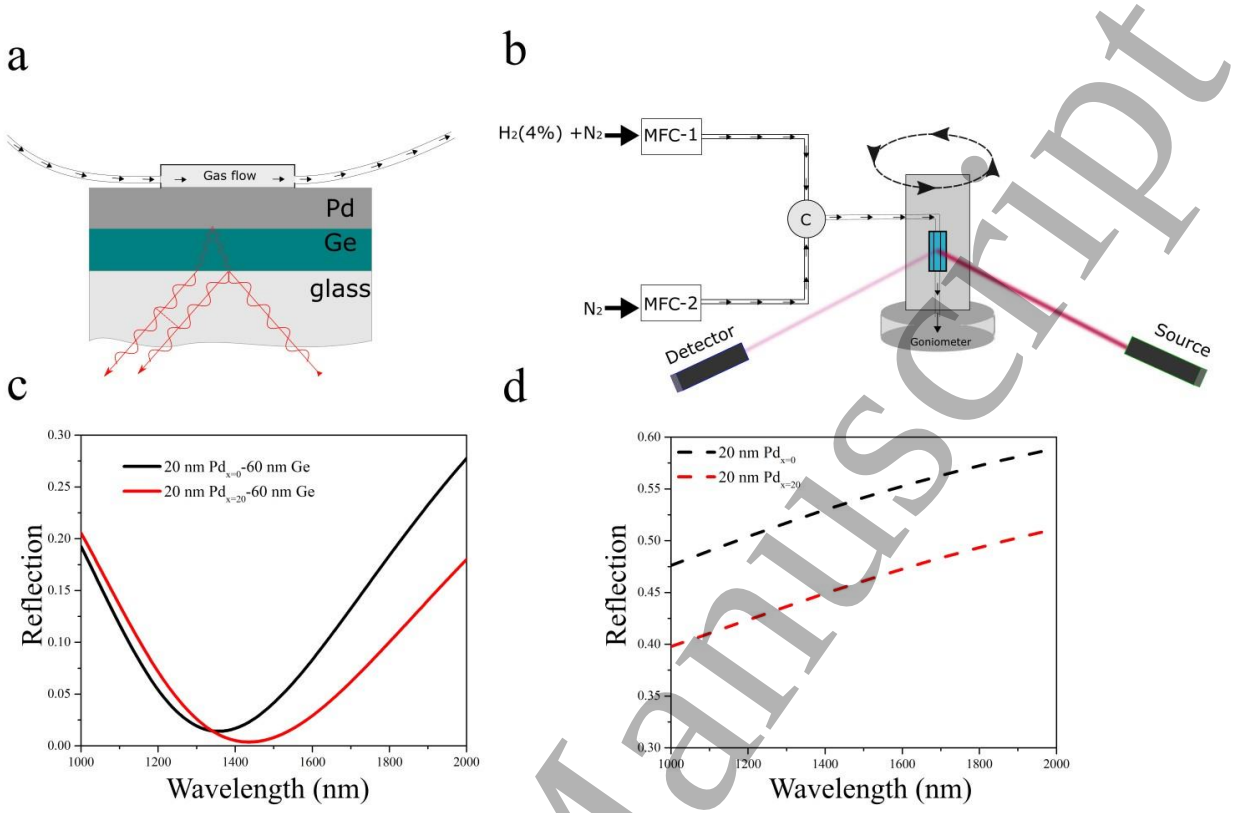

Fig. 1. : (a) A schematic of the optical coating sensor. The microfluidic channel is attached to the top of the Pd film to expose Pd to hydrogen. (b) The microfluidic channel is connected to two mass flow controllers (MFCs). One MFC controls the flow of nitrogen mixed with hydrogen (4% in concentration) and another MFC controls the flow of pure nitrogen. The sensor is placed on a variable angle ellipsometer to measure the angular reflectivity. Calculated reflectance of (c) Pd-Ge optical coating and (d) a Pd film, for hydrogen atomic ratio x=0 (black line), x = 20% (red line).

3- Theoretical background:

To understand the sensing mechanism, we investigate how the optical properties of our absorber depend on wavelength. The system of interest can be defined as a glass substrate with a refractive index n_0 (glass), a lossless dielectric layer with thickness h and refractive index n_D (Ge), and a lossy substrate with refractive index n_S+ik_S (Pd). Light is incident on the system with wavelength, λ, and incident angle, θ. Following the theory described in [14], we can express the conditions for perfect absorption as:

$$\tan \emptyset_D = \frac{(n_S - \gamma_0)\gamma_D}{k_S \gamma_0} = \frac{k_S \gamma_D}{\gamma_D^2 - n_S \gamma_0} \quad (1)$$

where $\gamma_0 = n_0/\cos\theta$, $\gamma_D = n_D^2/\sqrt{n_D^2 - n_0^2 sin^2\theta}$, and $\emptyset_D = 2\pi h n_D^2/(\lambda\gamma_D)$. The latter is the phase gain in one pass through the dielectric layer. Note that to derive the above expressions, we assumed $|n_0 \sin\theta/(n_S + ik_S)|^2 \ll 1$, which is valid for the system under consideration. Both equalities in the equation above must be simultaneously satisfied for perfect absorption to occur. In the simplest scenario, we can ignore the dependence of n_0 and n_D on λ, so that we can rewrite the conditions for perfect light absorption directly in terms of λ_{min}:

$$\lambda_{min} = \frac{2\pi h n_D^2}{\gamma_D \left[m\pi + \tan^{-1}\left(\frac{(n_S - \gamma_0)\,\gamma_D}{k_S \gamma_0}\right)\right]}, \quad (2)$$

where m is an integer. Equation (2) shows that as n_S and k_S vary, the value of λ_{min} where perfect absorption takes place will also shift. Even if the variation in n_S and k_S does not perfectly preserve in Eq. (2), the equation still serves as an approximation for how λ_{min} changes. Clearly, changes in n_S and k_S of the metallic substrate can lead to a strong shift in λ_{min}. In addition, for a thin-film light absorber, the absorption linewidth depends on the reflectance from each interface where broader absorption modes are obtained for metallic films with lower reflectance [31]. To confirm our expectations, we performed transfer matrix method calculation to calculate the reflection of the proposed Pd-Ge optical coating for hydrogen atomic ratio x=0 and 20% (**Fig. 1c**). The calculated shift in reflection minimum λ_{min} is 90 nm and the full width at half maximum has increased by ~ 200 nm. Conversely, the traditional direct measurement of the change in reflection of a Pd film, monitored from the glass slide, would lead to ~ 8% change in reflection as shown in **Fig. 1d**. The incident light is p-polarized for all the calculations and measurements presented in this manuscript. We note here that the thin film interference-based hydrogen sensing differs from hydrogen sensing by coating Pd or other chemochromic oxides coated onto the tip or along the length of an optical fiber that is later detected by means of interferometry [31]. In the latter case, Pd coats a small portion of the fiber and upon hydrogen exposure and lattice expansion, the fiber's effective optical path length changes [15].

4- Result and discussion

Fig. 2a shows the measured reflection spectrum of the optical coating over the wavelength range 1000-2000 nm at 25^0 (top panel), 35^0 (middle panel), and 45^0 (bottom panel). We first note that λ_{min} occurs at similar wavelengths regardless of the incident angle. After introducing H_2 at 4% concentration, we see a clear shift in λ_{min}. The total shifts in λ_{min} are $46 \pm 2nm, 47 \pm 2nm,$ and $45 \pm 2nm$, at $25^0, 35^0$, and 45^0, respectively. The angle-independent sensitivity is an interesting property of the demonstrated sensor.

Fig. 2b and **2c** show contour maps of the angular reflectance for our sensors exposed to N_2 only and to H_2 (4% in N_2), respectively. In addition to the wavelength shifts, the FWHMs of the absorption modes significantly increase in the presence of H_2. The changes in the FWHM are $195 \pm 4nm$, $186 \pm 4nm$, and $228 \pm 4nm$, at 25^0, 35^0, and 45^0 respectively. The change in the FWHM can be measured by monitoring changes in the reflection intensity of a broadband NIR light source, e.g., using Tungsten Halogen and Krypton lamps. Sensors that rely on changes in the intensity may offer a cheaper alternative as they do not require using a spectrometer. For a broadband detector, the reflected power can be calculated as

$$P = \int \frac{h\,c}{\lambda}\, R(\lambda)\, d\lambda \tag{3}$$

where h and c are the Planck's constant and speed of light and $R(\lambda)$ is the spectral reflection of the sample. We can then calculate the percent power difference before and after introducing the hydrogen as follows:

$$\Delta P = \frac{P_{N2} - P_{H2}}{P_{H2}} \times 100 \tag{4}$$

Where P_{N2} and P_{H2} are the reflected power from the sensor before and after introducing hydrogen, respectively. The increase in the FWHM due to introducing hydrogen is tantamount to a decrease in the total reflected power. The calculated ΔP is ~ 25%, 28%, and

33% for a hydrogen concentration of 4% and an incident angle of 25°, 35°, and 45°, respectively.

We note that the change in the FWHM of the optical coating hydrogen sensor is an additional advantage over Fabry-Perot cavity hydrogen sensor which shows small overall change in the FWHM[15]. Furthermore, Fabry-Perot hydrogen sensors rely on cavity resonances which requires a dielectric with an optical thickness of at least $\lambda/2$ which requires excessively thick dielectric films when operating at longer wavelengths.

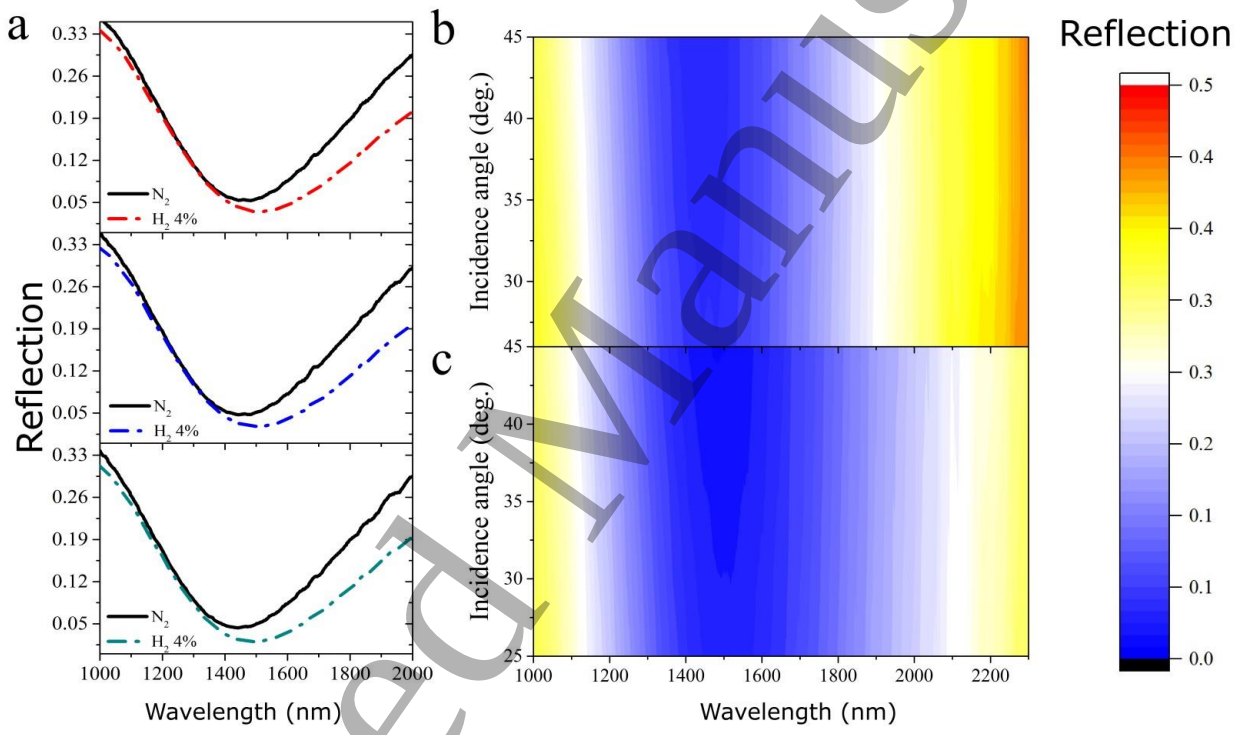

Fig. 2. (a) Reflection measurements for the optical absorber before and after introducing hydrogen with C= 4% for three different incident angles 25°, 35°, and 45°. A contour plot of the angular reflection shows the angular reflection of the absorber for (b) C = 0% and (c) C = 4%. The FWHM increases significantly after introducing hydrogen for all incident angles.

Fig. 3a shows the shift in reflection at an incidence angle of 45^0 as a function of hydrogen concentration. We obtained shifts of 6.5 nm, 18.6 nm, and 44 nm at concentrations of 0.7%, 2%, and 4%, respectively. We note that the lowest hydrogen concentration used was determined based on the MFC control range and do not represent the lowest concentration that can be detected. For comparison, previous works showed ultrasensitive optical

hydrogen sensing with ~ 2.5 nm shift in wavelength for 0.6% hydrogen concentration[32]. In our work, we demonstrate 6.5 nm shift for 0.7%.

We also studied the hysteresis behavior of the sensor. In general, when Pd forms a hydride, a mechanical energy barrier is created due to the coherency strain produced by the lattice expansion of the hydride phase [6]. This barrier prevents the release of hydrogen atoms situated inside the hydride lattice to recover the original Pd structure. **Fig. 3b** shows a hysteresis plot for the shift in λ_{min} at different H_2 concentrations (0%, 0.7%, 2% and 4%) and 45^0 incidence angles. Each measurement presented is extracted from the steady state reflection spectrum which was obtained after ~ 12 minutes for each concentration. The λ_{min} is found to be higher when the H_2 concentration is decreased than when the H_2 concentration is increased. We suggest that the hydrogen content or stoichiometries in terms of x in the PdH_x are different during the forward and reverse cycles of exposing to different H_2 concentrations, with the stoichiometry being higher in the reverse cycle because of the aforementioned mechanical energy barrier to deintercalation from coherency strain. We note here that heating the sensor to higher temperatures could limit or eliminate the observed hysteresis, however, on the expense of minimizing the sensitivity[33,34]. Moreover, using Pd alloys was shown to minimize the hysteresis significantly, e.g., using Pd Au alloys[35,36]. The existence of coherency strain, however, did not affect the overall performance of our sensor as the absorption mode relaxed to the initial λ_{min} when the H_2 concentration was decreased to zero (pure N_2).

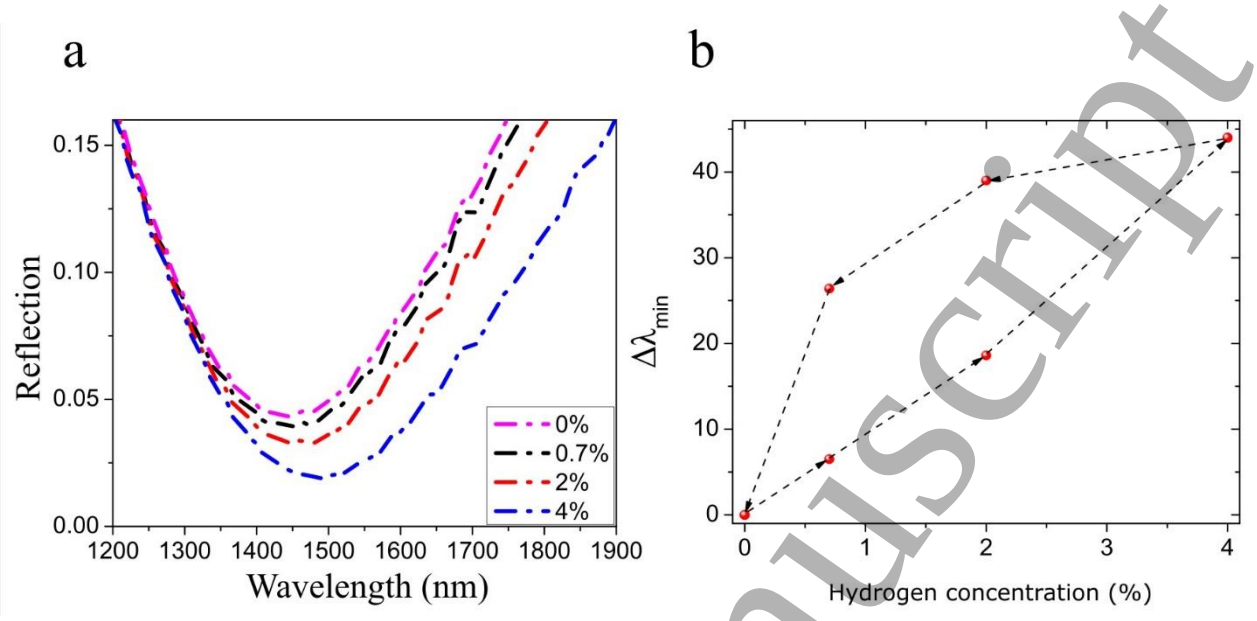

Fig. 3. (a) Reflection of the absorber as a function of hydrogen concentration. (b) Sensor response to hydrogen concentrations (0.7% - 4%) showing hysteresis behavior in reflectivity minimum, λ_{min}.

5- Conclusion

In summary, we developed an ultrathin film optical coating for hydrogen sensing. The sensor consists of an antireflective, absorptive Pd film. The change in the antireflection properties in terms of reflection minimum and FWHM enabled the detection of low hydrogen concentrations. The sensor shows similar overall shift in reflection minimum over a broad range of incidence angles. Hysteresis in the reflection minimum was found arising from a mechanical energy barrier to deintercalation but did not lead to degradation in the sensor performance. The hysteresis issue can be potentially mitigated by employing different types of Pd alloys as substrates. Moreover, using Pd alloys with higher hydrogen diffusion coefficients or using a substrate consisting of Pd nanowire mesh[37] can provide a sensor with a short response time.

Acknowledgements

G.S. received funding from the Ohio Third Frontier Project "Research Cluster on Surfaces in Advanced Materials (RCSAM) at Case Western Reserve University" and the GU Malignancies Program of the Case Comprehensive Cancer Centre and was supported in part by the National Science Foundation, Grant No. DMR-1708742. U.A.G. acknowledges National Heart

Lung and Blood Institute R01HL133574, and National Science Foundation CAREER Award #1552782. This article's contents are solely the responsibility of the authors and do not necessarily represent the official views of the National Institutes of Health.

Disclosures

The authors declare no conflicts of interest.

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