Registration of long-range surface plasmon resonance by angle-scanning feedback and its implementation for optical hydrogen sensing

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\textbf{Abstract.} An optical technique devised for the detection of the ultrasharp angular resonance of long-range surface plasmons (LRSPs) is described. The LRSPs propagate along an 8 nm-thick palladium (Pd) film deposited on a one-dimensional photonic crystal structure and bordering a gas environment at another Pd film interface. At such a small metal film thickness, the scattering attenuation losses prevail over dissipation losses inside the film and we use this scattering as an input signal to pick up the angle of the surface plasmon resonance by a closed feedback loop via an angle-scanning piezomirror. As an implementation of this technique, we detected a 0.5\% hydrogen concentration in nitrogen at room temperature with a signal/noise ratio of approximately 100 and response and recovery times of about 5 and 15 s, respectively.

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1. Introduction

Hydrogen-gas-leak detectors are needed in many hydrogen applications, where rapid detection of hydrogen leaks below the lower explosive limit (LEL) of \( \sim 4\% \) in air is desirable. Optical detection methods have the advantages that they can be used for remote sensing and they have lower ignition risks near the sensing area in potentially explosive atmospheres. Unfortunately, the molecular structure of \( \text{H}_2 \) makes the selective detection of hydrogen by standard optical spectroscopy methods very difficult: \( \text{H}_2 \) is a homonuclear diatomic molecule and has no dipole vibrational transition in the infrared (IR) range, whereas the electronic transitions of hydrogen lie in the vacuum ultraviolet range. At the same time, Raman and coherent Raman spectroscopy methods are costly, require relatively high laser power, and may be unsafe in explosive environments.

For these reasons the selective measurement of hydrogen is still a challenging technological problem in spite of the wide range of instruments (including commercial ones) that are currently available. In these instruments, a palladium film is commonly used as the selective layer, in conjunction with a range of transducers, such as thin-film resistors [1], nanoparticle resistors [2]–[4], Schottky diodes [5, 6], metal-oxide-semiconductor structures [7] and, certainly, optical sensors [8]–[12], including plasmonic [13] and nanoplasmonic ones [14].

Palladium is able to absorb up to 900 times its own volume in hydrogen in a reversible process, where the amount of hydrogen soluble in Pd is dependent on the temperature and partial pressure of the hydrogen. Hydrogen uptake by palladium strains the Pd lattice, leading to a volumetric expansion that reaches equilibrium for a given hydrogen concentration in the environment around the material [15]. This volumetric expansion leads to an increase in the thickness of the Pd film on the one hand and a decrease in the real and imaginary parts of the palladium refractive index (RI) on the other hand. In surface plasmon (SP) sensors, these changes lead to a shift in the surface plasmon resonance (SPR) position.

2. Long-range SPs (LRSPs) at the metal–gas interface

An SP is an excitation of a bound electromagnetic (EM) mode near a metal–dielectric interface [16]. Metals such as silver and gold are the most popular substrates for SP excitation due to their comparatively low losses in the visible spectral range. Palladium, on the other hand, is a lossy metal, with the imaginary part of its dielectric susceptibility being rather large and the SP propagation length on Pd in the visible spectral range being very short (\( \leq 1 \mu\text{m} \)).
It is possible to increase the SP propagation length and, consequently, the SPR sensitivity by using LRSPs. LRSP can be excited in a thin metal film, imbedded between two dielectrics with identical RIs [17]–[21]. This requirement to match the RIs on both sides of the metal film poses serious complications for the practical employment of LRSPs for sensing in liquids and gaseous environments. For example, in gases \((n_e \simeq 1)\), a freely suspended thin metal film is required to match the RIs on both sides and consequently ultrathin membranes are currently the only option as its support [22].

In the work [23], it was shown that this RI matching requirement may be circumvented by using a one-dimensional (1D) photonic crystal (PC) instead of an RI matching layer to obtain a minimum EM field strength inside the metal film. The 1D PC is a simple periodic multilayer stack. Such a 1D PC can exhibit photonic band gaps where the propagation of optical EM waves is forbidden. By changing the band gap parameters by modifying the thicknesses of alternating layers in the stack, the LRSP propagation can be excited in the terminal metal layer, bordering an external medium with any RI, including \(n_e \simeq 1\). The use of the 1D PC instead of an RI matching layer to obtain a minimum EM field strength inside the metal film permits us to excite LRSPs along the metal nanofilm bordering arbitrary environments (including gaseous environments). Moreover, this increase takes place even for lossy metals such as Pd, which recommends this structure as a promising system for hydrogen detection [24].

The long-range surface waves in lossy metals were obtained so far only in a ‘quasi-symmetric’ scheme, where a matching fluid was used to match the RIs on both sides of the metal film [25]. A resonance width of about \(0.15^\circ\) (\(\sim 2.6 \times 10^{-3}\) rad) was observed in thin vanadium and palladium films at \(\lambda = 3.391 \mu m\) [19]. But this ‘quasi-symmetric’ scheme will not work if \(n_e \sim 1\) near one interface and its implementation for sensing experiments seems to be difficult if not impossible. In contrast, in our structure, the unique wavelength tunable properties of our 1D PC permit us to achieve long-range propagation by simple tuning of the laser wavelength [23, 24].

The principal reason for the long-range plasmon propagation is the presence of the minimum electric field strength inside the thin metal film, which is the result of destructive interference between SPs from both film interfaces. It is because of this field minimum inside the film that LRSP propagation is possible even along lossy metals such as Pd. It may be shown that the thinner is the final metal layer, the smaller the EM field is inside this layer (though the maximum EM field still occurs at the external interface of the layer). On the other hand, at a very small metal film thickness (\(\sim 10\) nm), the effective RI of the LRSP is approaching the RI of the external medium \((n_{LRSP} \rightarrow n_e \simeq 1);\) see equation (1) from [23]) and, as a result, the scattering attenuation losses of LRSPs become prominent.

In this work, we present a hydrogen detection system that uses this LRSP scattering as an input signal to pick up the SPR angle in the Pd nanofilm on 1D PC. The use of LRSP scattering as the input signal is possible because the scattering losses become a considerable attenuation channel of the LRSPs, while the dissipation losses in the metal film are reduced due to the presence of the minimum electric field strength of the LRSP inside the thin metal film [23]. Detection of the LRSP scattering is possible by using a simple photodiode, while a position-sensitive photodetector is needed for SPR dip registration at total internal reflection in standard SPR techniques.
3. Experimental setup

The 1D PC structure used in the experiments is as follows: substrate/(HL)^14H’M/air, where H is a Ta_2O_5 layer with a thickness d_2 = 112.8 nm, L is an SiO_2 layer with d_1 = 155.0 nm, H’ is a Ta_2O_5 layer with d’_2 = 103.4 nm, and M is the palladium layer with d_3 = d_M = 8 nm. The prism and the substrate were made of BK-7 glass. The Ta_2O_5/SiO_2 multilayer and palladium film are deposited by magnetron and cathode sputtering, respectively. The RIs of the substrates Ta_2O_5, SiO_2 and Pd are, respectively, n_0 = 1.513, n_2 = 2.076, n_1 = 1.455, and n_3 = n_M = 1.9 + 4.8i.

A sketch of the experimental setup is shown in figure 1: a parallel light beam from a fiber-coupled laser diode (λ = 737.7 nm, P = 0.74 mW) excites the LRSPs in the 1D PC structure at a resonance angle θ_0 through an angle-scanning mirror. The angle-scanning piezomirror modulates the incident angle around the resonance angle with its natural frequency (∼1.3 kHz) of rotational vibrations of the piezomirror by the value of Δθ_0. The collected scattering light has its maximum precisely at the SPR angle θ^{SPR}_0 and diminishes, while the angle-scanning mirror deflects the incident excitation angle from the resonance (see the inset outlined by dots in figure 1). As a consequence of this feature, the palladium surface flashes at the double modulation frequency (∼2.6 kHz) when the system is precisely tuned to the SPR angle, while a signal of the first harmonic (∼1.3 kHz) appears when the SPR angle and the excitation angle are untuned. The scattering light from the LRSPs is collected on a photodiode by a lens.
The lock-in amplifier picks out, detects and amplifies the signal of the first harmonic and then this rectified signal (after inverting) is fed back to the angle-scanning piezomirror.

As a result, we have a closed negative feedback loop that picks up the SPR angle. If the SPR angle changes (for example, due to an increase in the Pd nanofilm thickness during hydrogen injection), the feedback loop changes the voltage at the piezomirror to tune the system to a new SPR angle. The voltage at the piezomirror is our useful signal, which is recorded by a computer via an analog–digital converter. The voltage–angle conversion ratio of the angle-scanning piezomirror is \( \delta \theta = \frac{\partial \theta}{\partial V} \times \Delta V \), where \( \partial \theta / \partial V \simeq 2 \times 10^{-5} \text{ rad V}^{-1} \), except for the frequency range near 1.3 kHz, where the natural resonance of rotational vibrations of the piezomirror occurs and where the coefficient \( \partial \theta / \partial V \) is \( Q = 15 \) times as great.

It should be noted that the distance between the piezomirror and the 1D PC is small in our system \( (s \simeq 5 \text{ cm}) \), so the light beam displacement across the palladium surface during mirror scanning is negligible. For instance, in our experiments, the double amplitude of the natural rotational vibrations of the piezomirror excited by the 1.3 kHz generator is about \( \Delta \theta \simeq 6 \times 10^{-4} \text{ rad in air} \), which correlates with a laser beam’s natural divergence in air of \( \sim 5 \times 10^{-4} \text{ rad} \) (the angular width of the LRSP resonance in this system is also approximately the same [24]). Therefore, the displacement at a frequency 1.3 kHz is \( \Delta l \simeq s \Delta \theta / (n_0 \cos \theta_0) \simeq 26 \mu \text{m} \), which is less than both the diameter of the parallel light beam \( (\sim 1.5 \text{ mm}) \) and the LRSP propagation length across the palladium film in this system \( (L_{1/e} \simeq 180 \mu \text{m}) [24]) \).

### 4. Hydrogen detection

To verify the sensitivity of our system to hydrogen and to compare it with existing hydrogen sensors, we present experimental data showing changes in the feedback voltage at the piezomirror in response to exposure to 0.5% hydrogen. The data are shown in figure 2. The measurements were performed in a nitrogen environment at atmospheric pressure and room temperature \( (20^\circ \text{ C}) \). The 0.5% \( (\nu/\nu) \) hydrogen was added to a gas chamber attached to the 1D PC structure with a terminal Pd layer. The time per point was about 0.5 s (while the lock-in integration time is \( \sim 0.1 \text{ s} \) and no posterior data averaging or smoothing was done. One can see that the response time following hydrogen injection was about 5 s and the recovery time was about 15 s. This was a rather fast response among palladium sensors and did not seem to be diffusion limited, because the diffusion time of hydrogen in an 8 nm-thick Pd film should be less than 1 \( \mu \text{s} \) (since the diffusion coefficients are \( D_a = 10^{-7} \text{ cm}^2 \text{s}^{-1} \) and \( D_\beta = 10^{-6} \text{ cm}^2 \text{s}^{-1} \) for \( \alpha \) and \( \beta \) phase PdH). So this time response is most likely limited by the surface processes, as the surface is not atomically clean.

From figure 2, one can see that the noise floor of the base line is about \( \delta V = \text{std}(V) \simeq 4 \times 10^{-2} \text{ V} \) (where std is the standard deviation) for our 0.1 s lock-in integration time. Therefore, we detected 0.5% hydrogen with a signal/noise \( (\text{S/N}) \) ratio of about 100. For the 1 s lock-in integration time, this would correspond to a noise floor equal to \( \delta V \simeq 1.3 \times 10^{-2} \text{ V} \), which is \( \delta \theta \simeq 2.6 \times 10^{-7} \text{ rad} \) in angle units or \( \delta n \simeq 3 \times 10^{-7} \) in RI units.

The main physical reason for the LRSP resonance shift in response to hydrogen injection is the increase in Pd film thickness. The decrease in the real and imaginary parts of the palladium RI plays a minor role here, although it gives an important contribution in the response of ordinary SPR [13] or optical [8, 9, 11] hydrogen sensors. The influence of the palladium nanofilm parameters on the position of the LRSP resonance is illustrated in figure 3. The red dashed line and the green dash–dot line separately represent the effects of
Figure 2. Changes in the feedback voltage on the piezomirror in response to hydrogen injection.

Figure 3. Modeling of the changes in the initial LRSP resonance curve (black solid line, $d_M = 8.08$ nm, $\epsilon_M = -19.42 + 18.46 i$) in response to: increase of the palladium film thickness by 3.54% (red dashed line, $d_M = 8.37$ nm, $\epsilon_M = -19.42 + 18.46 i$); decrease of the palladium RI by 20% (green dash–dot line, $d_M = 8.08$ nm, $\epsilon_M = -15.53 + 14.77 i$); increase of the palladium film temperature by 100 K (blue dotted line, $d_M = 8.09$ nm, $\epsilon_M = -19.39 + 25.8 i$).
α-to-β phase transition of PdH in response to simulated 4% hydrogen injection, where the shift of the red dashed line is the result of the 3.54% increase of the Pd lattice constant at such a transition, whereas the shift of the green dash-dot line is a result of the 20% decrease of the Pd RI at such a transition [9]. The shift from the initial black solid line to the dotted blue line is the result of modeling the response to a 100 K increase of the Pd film temperature, which leads to a small increase of the film thickness and to a considerable increase of the damping of the conduction electrons due to the increased number of thermal phonons.

From modeling results presented in figure 3, one can see that this 1D PC structure is more sensitive to the Pd film thickness changes compared to the Pd RI changes. The reason is as follows: although the maximum of the EM field of LRSPs occurs at the external interface of the film as usual, there is a minimum of the EM field strength inside the Pd film, which makes LRSPs in this system less sensitive to changes in the film RI. This feature may make this system less sensitive to temperature fluctuations in comparison with resistive [1] Pd sensors due to the next physical reason: in resistive Pd sensors the changes of the temperature produce a (false) signal through the temperature coefficient of resistivity, which is of the order of $\sigma_{Pd} \approx 4 \times 10^{-3} \text{K}^{-1}$, while a (false) signal in the presented hydrogen sensor appears through the temperature expansion coefficient of the Pd film, which is of the order of $\nu_{Pd} \approx 1.7 \times 10^{-5} \text{K}^{-1}$ (we neglect temperature stabilization methods in both examples and consider a hydrogen-free film). Experimental check of the temperature sensitivity of the present sensor will be done elsewhere.

5. Conclusion

LRSPs have been excited in a Pd nanofilm bordering a 1D PC on one side and a gas environment on the side. The ultrasharp plasmon resonance in this system lets us measure changes in the Pd nanofilm thickness as a result of hydrogen injection with a fast time response. In contrast with several implementations of scanning mirrors in standard SPR systems [26]–[28], where light reflected from the prism is used for measurements, the long-range propagation of SP in our structure permits us to use LRSP scattering as the input signal for the feedback loop. The second important difference is the ultrasharp angular width of the LRSP resonance in our system (which is comparable to natural laser beam divergence). As a result, a small value of angular scanning is needed for 100% modulation. These differences permit us to pick up the SPR angle with a precision of $2.6 \times 10^{-7} \text{rad per } \sqrt{\text{Hz}}$. One eighth of the LEL hydrogen concentration was detected with an S/N ratio of $\sim 100$. An additional benefit of the long-range propagation is that there is a reduced necessity for the light beam to be spatially stationary at the probing surface, which simplified our setup.

The presented scheme for tracking the LRSP coupling angle via the LRSP scattering will be useful especially for Pd films with strong scattering, e.g. for a layer consisting of Pd nanoparticles, where the registration of the LRSP resonance dip in the reflection may be hampered. The replacement of the continuous Pd nanofilm by the layer of Pd nanoparticles may considerably improve the durability of the hydrogen sensor as it prevents the Pd film from decrepitating into grains upon cycling exposure to H$_2$. 

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