

Surface plasmon resonance hydrogen sensor based on metallic grating with high sensitivity

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Abstract: High sensitivity is obtained at larger resonant incident angle if negative diffraction order of metallic grating is used to excite the surface plasmon. A highly sensitive grating-based surface plasmon resonance (SPR) sensor is designed for the hydrogen detection. A thin palladium (Pd) film deposited on the grating surface is used as transducer. The influences of grating period and the thickness of Pd on the performance of sensor are investigated using rigorous coupled-wave analysis (RCWA) method. The sensitivity as well as the width of the SPR curves and reflective amplitude is considered simultaneously for designing the grating-based SPR hydrogen sensor, and a set of optimized structural parameters is presented. The performance of grating-based SPR sensor is also compared with that of conventional prism-based SPR sensor.

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References and links

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1. Introduction

In recent years, the utilization of hydrogen as energy source has attracted much attention in the scientific community, owing to its high calorific power. Moreover, it's clean, sustainable and abundant. On the other hand, hydrogen is very volatile and extremely flammable, which make it complex to handle and store. A leakage of hydrogen more than 4% (the lower explosive limit, LEL) in air would lead to an easily ignited explosive atmosphere. For this reason, many hydrogen sensors have been developed for monitoring hydrogen concentration [1-4]. A thin palladium (Pd) or Pd alloy layer is commonly used as the transducer since it allows the selective detection of hydrogen.

Surface plasmon resonance (SPR) phenomenon was first used for sensing technology in 1982 [5]. Since then SPR sensing technology receives continuously growing attention from scientific researchers, due to its advantages of high sensitivity, label-free, real-time and rapid detection. During the last two decades, it has made great progress in the development of instrumentation and practical applications [6-10]. Most of the SPR sensors use the attenuated total reflection (ATR) method to excite the surface plasmon wave. The application of metallic diffraction grating for SPR sensing is advocated by Cullen et al. [11]. Since then, SPR sensors based on grating are studied as an alternative to ATR systems [12-15]. In this work, we design a novel SPR hydrogen sensor using a Pd-coated gold sub-wavelength grating. Rigorous coupled-wave analysis (RCWA) method is applied to study the influence of grating parameters and the thickness of Pd on the performance of grating-based SPR hydrogen sensor. And a set of optimized structural parameters is presented.

2. Grating-based SPR sensor

Surface plasmon wave (SPW) is the binding electromagnetic wave launched from the collective oscillation of the surface charge density at the metal-dielectric interface. It can be resonantly excited by TM-polarized optical field in the case of phase match condition is fulfilled. The wave vector can be calculated from the dispersion relation of SPW at the metal-dielectric interface as following:

$$k_{SPW} = k_0 \sqrt{\frac{\epsilon_m n_d^2}{\epsilon_m + n_d^2}} \quad (1)$$

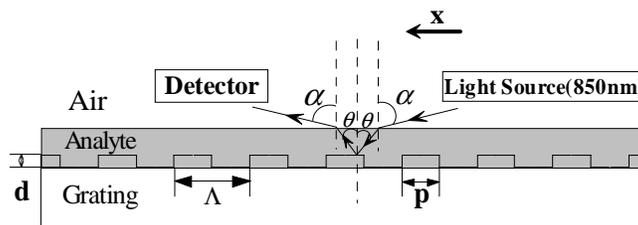


Fig. 1. Illustration of SPR sensor based on metallic diffraction grating.

where k_0 is the free space wave vector of optical wave, ϵ_m is the permittivity of the metal ($\epsilon_m = \epsilon_{mr} + i\epsilon_{mi}$), and n_d is the refractive index of the dielectric. The horizontal component of the incident light wave vector $k_x = k_0 n_d \sin\theta$, where θ is the incident angle. Because SPW is an evanescent electromagnetic wave, its propagation constant is always greater than that of propagating light in the dielectric material. Prism or grating coupling is commonly used optical phase-matching technique in SPW excitation.

As shown in Fig. 1, the diffraction at a metallic diffraction grating provides excess in-plane momentum to compensate the wave vector mismatch between the incident wave and SPW. The incident plane of TM light is oriented perpendicular to the grooves of gold grating, Λ is the period of grating, p is the ridge width of grating, d is grating depth, $f = p/\Lambda$ is the duty cycle. The incident wavelength λ is fixed at 850nm, and $\epsilon_{\text{gold}}(850\text{nm}) = -31.151 + 2.198i$ [16]. The match condition of wave vector is expressed as:

$$\pm k_0 \sqrt{\frac{\epsilon_m n_a^2}{\epsilon_m + n_a^2}} = k_0 n_a \sin \theta_{\text{res}} + m \frac{2\pi}{\Lambda} \quad (2)$$

where θ_{res} is the resonant angle of incidence, n_a is the refractive index of analyte which in contact with the surface of grating, m is an integer represent the diffraction order. Sign '+' and sign '-' correspond to $m > 0$ and $m < 0$ respectively. Equation (2) indicates the resonant angle θ_{res} is a monotonic function of refractive index n_a , therefore, the grating can perform as a refractive index sensor in angular interrogation, similarly to the typical prism-based setup but in a more compact structure. It is easy to deduce the derivation of $d\theta_{\text{res}}/dn_a$ from Eq. (2), which indicated the sensitivity of the sensor:

$$S_G = \left| \frac{d\theta_{\text{res}}}{dn_a} \right| = \left| \frac{1}{n_a \cos \theta_{\text{res}}} \left[\pm \left(\frac{\epsilon_m}{\epsilon_m + n_a^2} \right)^{\frac{3}{2}} - \sin \theta_{\text{res}} \right] \right| \quad (3)$$

It is very interesting that the sensitivity is expressed as a function depending only on the resonant angle, not on the diffraction order m .

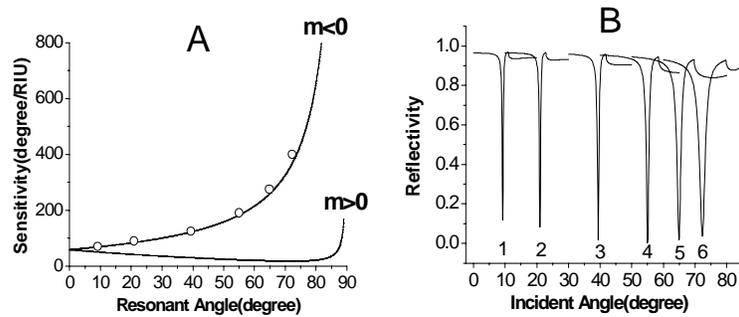


Fig. 2. (A). Sensitivity of the resonant angle of grating-based SPR sensors versus the resonant angle of incidence ($\lambda = 850\text{nm}$, $n_a = 1.02$). The line is theoretical curve calculated using Eq. (3). The circles are the simulated results calculated using the rigorous coupled-wave analysis method (RCWA). The six circles from left to right correspond to six grating configuration: 1) $\Lambda = 700\text{nm}$, 2) $\Lambda = 600\text{nm}$, 3) $\Lambda = 500\text{nm}$, 4) $\Lambda = 450\text{nm}$, 5) $\Lambda = 430\text{nm}$, 6) $\Lambda = 420\text{nm}$. And $f = 0.9$, $d = 40\text{nm}$, $m = -1$ in all six configuration. (B) Angular SPR curves of the grating-based SPR sensor with different parameters. The curves are calculated using RCWA, and from left to right correspond to the above six grating parameters ($n_a = 1.02$).

The function of sensitivity on the resonant angle is curved in Fig. 2(A) for both cases of negative ($m < 0$) and positive ($m > 0$) diffraction order. The behaviors of these two cases are totally different: for $m < 0$, sensitivity goes higher quickly as the resonant angle increases especially in the condition of $\theta_{\text{res}} > 60^\circ$, theoretically, the sensitivity approaches to infinity at

$\theta_{\text{res}} = 90^\circ$. In the case of $m > 0$, sensitivity goes down from $\theta_{\text{res}} = 0^\circ$, then rise up as the resonant angle is very close to 90° . In any resonant angle, the sensitivity of $m < 0$ is always greater than that of $m > 0$, especially at large resonant angle, for example $\theta_{\text{res}} > 60^\circ$, the sensitivity can be improved by tens of times if we replace the positive diffraction order with negative diffraction order.

The choice of negative diffraction order can be made by controlling the grating period. Effectively excitation of plasmon generally requires $|\epsilon_m| \gg n_a^2$, therefore, the limitation on the grating period for both positive and negative diffraction order can be achieved from Eq. (2) as following:

$$\Lambda > \frac{m\lambda}{n_a} \quad (m > 0), \quad \frac{|m|\lambda}{2n_a} < \Lambda < \frac{|m|\lambda}{n_a} \quad (m < 0) \quad (4)$$

It is seen that negative diffraction order survived only in condition of some specific grating period. For example, the -1 diffraction order requires the grating period is limited within $\lambda/2n_a$ to λ/n_a . In the following discussion, we'll focus on this kind of sub-wavelength metallic grating and apply its -1 diffraction order into sensing. Using RCWA method, the angular SPR curves of the grating-based SPR sensor are calculated with different periods of $\Lambda = 700\text{nm}$, 600nm , 500nm , 450nm , 430nm , and 420nm (Fig. 2(B)). The surface plasmon dips are excited by -1 diffraction order. The resonant angle goes to bigger as the grating period decreases and the sensitivity increases quickly especially at large angle approaching 90° (the circles in Fig. 2 A)).

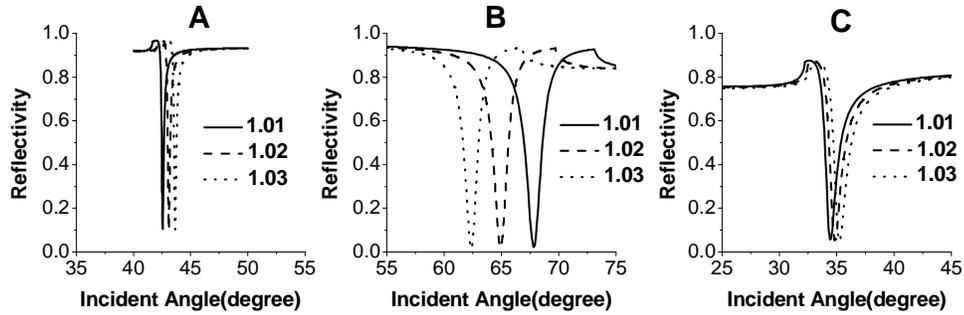


Fig. 3. (A). Angular SPR curves of the prism-based SPR sensor with three different refractive index of analyte: $n_a = 1.01, 1.02, 1.03$. The prism is made of BK7 glass, and the thickness of gold film deposited on the prism is 50nm . (B) Angular SPR curves of the -1 diffraction order grating-based SPR sensor with three different refractive index of analyte: $n_a = 1.01, 1.02, 1.03$. The structure parameters of gold grating are $\Lambda = 430\text{nm}$, $f = 0.9$, $d = 40\text{nm}$. (C) Angular SPR curves of the +1 diffraction order grating-based SPR sensor with three different refractive index of analyte: $n_a = 1.01, 1.02, 1.03$. The structure parameters of gold grating are $\Lambda = 1800\text{nm}$, $f = 0.7$, $d = 70\text{nm}$.

The performance of the grating-based SPR sensor is compared with the conventional prism-based SPR sensor. The angle dependence of reflectivity is calculated using the well-known Fresnel equations for the prism-based SPR sensor (Fig. 3(A)) and simulated by the RCWA method for the grating-based SPR sensor (Fig. 3(B), Fig. 3(C)). As the refractive index of analyte varies from 1.01 to 1.03, the resonant angle shifts 1.09° for the prism-based SPR sensor, -5.4° for the -1 diffraction order grating-based SPR sensor, and 0.8° for the +1 diffraction order grating-based SPR sensor. The sensitivity of the -1 diffraction order grating-based SPR sensor is about 5 times higher than that of the prism-based SPR sensor in gas detection, and about 7 times higher than that of +1 diffraction order grating-based SPR sensor.

Because the high sensitivity is achieved only at large incident angle close to 90°, the negative diffraction order grating SPR sensor is more applicable to gas than liquid sensor. As shown in Fig. 1, the incident angle onto the grating θ is limited by the refractive index of the analyte. Supposed the aqueous liquids have refractive indices near 1.33, or even larger, the total reflection critical angle between the liquid and air is about 48.6°(when $n_a=1.33$), and the incident angle at the surface of the grating θ can not exceed the critical angle (48.6°). Thus the sensitivity would be smaller than 154°/RIU, according to Fig. 2(A). Since the refractive indices of most gases are near 1.0, the incident angle at the surface of the grating can reach near 90°, and much higher sensitivity can be obtained. So we'll discuss only the gas sensing application of the negative diffraction order grating-based SPR sensor in the following.

3. Grating-based SPR hydrogen sensor

In order to apply the grating-based SPR sensor to hydrogen detection, it is necessary to coat Pd film on the surface of gold grating. The Pd film deposited on the surface of grating is used as the transducer. The modification of the SPR is due to variation in the permittivity of Pd in contact with gaseous hydrogen. The absorption and desorption of hydrogen in a thin layer of Pd leads to reversible hydride PdH_x, where x is the atomic ratio H/Pd. The absorption of hydrogen can be related to a crystallographic phase transition. A lot of physical quantities change significantly during the phase transition, such as complex permittivity. The effects of the absorption of hydrogen on the complex permittivity of Pd can be represented by the following empirical equation [3]:

$$\varepsilon_{\text{Pd},c\%H_2} = h(c\%) \times \varepsilon_{\text{Pd},0\%H_2} \quad (5)$$

where $\varepsilon_{\text{Pd},0\%H_2}$ is the complex permittivity of the pure Pd layer, $\varepsilon_{\text{Pd},0\%H_2}(850\text{nm}) = -23.785 + 22.708i$ [17]. $h(c\%)$ is a nonlinear function decreasing with hydrogen concentration $c\%$ and taking values less than 1. At normal conditions, $h(4\%) = 0.8$. When the Pd-coated gold grating exposed to hydrogen with different concentration, the permittivity of Pd layer changed. Then changes in resonant angle can be observed. Thus a grating-based SPR hydrogen sensor is presented.

For an angular-interrogation SPR sensor, resonant angle shift, reflectance amplitude and FWHM of SPR curves should be considered simultaneously in designing. Narrower FWHM and larger reflectance amplitude are desired because a deeper and narrower resonance dip allows efficient detection of the resonant shift. [9,] Thus we study the influence of grating period and the thickness of Pd on shift of resonant angle as well as FWHM and reflectance amplitude of the SPR curves to optimize performance of SPR sensor. The influence of the period of grating Λ has been investigated in section 2. When Λ changes from 700nm to 420nm, the resonant angle shifts to large value, and the sensitivity becomes much larger (from 70°/RIU to 400°/RIU), but the FWHM of SPR curves increases and the reflectance amplitude decreases (Fig. 2). So the period at 430 nm is selected for its relative narrower FWHM, larger sensitivity and reflectance amplitude.

Then we investigated the influence of the thickness of Pd t . The values of Λ , f , d are fixed at 430nm, 0.9, 40nm respectively and thickness t varies from 2nm to 14nm. Figure 4(A) shows the SPR curves with different values of thickness t . Figure 4(B) gives the variation of $\Delta\theta_{\text{res}}$ and FWHM of SPR curves with t . $\Delta\theta_{\text{res}}$ is the resonant angle shift while the hydrogen concentration increasing from 0 to 4%. In our simulation, the change of refractive index between the air with a hydrogen concentration of 0 and 4% is ignored because it's quite insignificant, comparing to that of Pd layer. The simulated results show that the FWHM of SPR curve increases and reflectance amplitude decreases as t enlarges. The increased damping can be understood in terms of the absorption of light power of Pd film whose imaginary part of permittivity is quite high. On the other hand, $\Delta\theta_{\text{res}}$ becomes larger when t increases, as shown in Fig. 4(B). We define a "figure of merit" (FOM) in order to directly compare the overall performance of this SPR hydrogen sensor:

$$\text{FOM} = \frac{\Delta\theta_{\text{res}}}{\text{FWHM}} \times \Delta R \quad (6)$$

where ΔR is reflectance amplitude of SPR curve. The variation of FOM with the thickness of Pd is given in Fig. 4(C). So the thickness 8nm is selected. Such a small thickness of Pd can provide fast and efficient response for the detection of hydrogen. Nevertheless, it may only be used to detect low concentration of hydrogen.

So the final structural parameters are selected as $\Lambda=430\text{nm}$, $f=0.9$, $d=40\text{nm}$, $t=8\text{nm}$. The resonant angle shift is 0.51° , while the hydrogen concentration increasing from 0 to 4%. In practice, the accuracy of angle measurement is 0.0001° for the state-of-art SPR sensor instrument (SPR 670, Nippon Laser & Electronics Lab) [18,], which leads to a detection limit of the hydrogen concentration on the order of 0.001%. It is much better than that of reported intensity-interrogation hydrogen sensor (0.1%) [3, 4, 19].

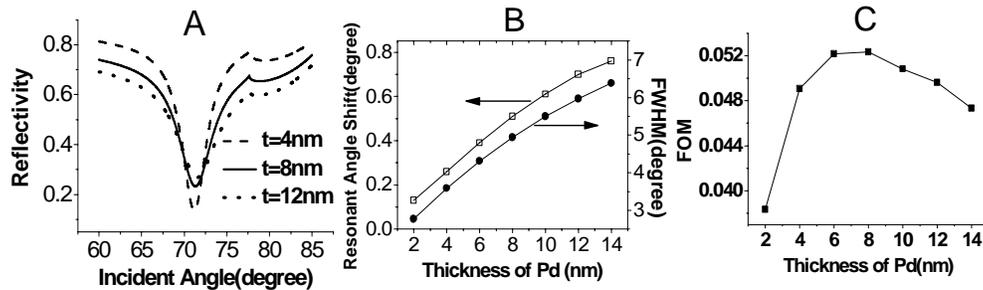


Fig. 4. (A). Angular SPR curves for different t values when sensor is exposed to air with a hydrogen concentration of 0. (B). The variation of $\Delta\theta_{\text{res}}$ and FWHM of SPR curves with thickness t . (C). FOM depend on thickness t . The values of Λ , f , d are fixed at 430nm, 0.9, 40nm respectively and t varies from 2nm to 14nm.

4. Conclusion

In summary, a highly sensitive SPR sensor using a Pd-coated metallic diffraction grating is designed for hydrogen sensing. The influences of the structural parameters on the sensitivity, reflectance amplitude and FWHM of SPR curves are investigated using RCWA. Higher sensitivity could be obtained at larger resonant angle by adjusting the structural parameters of grating. And it can be much larger than the sensitivity of prism-based SPR sensor. Resonant angle shift, FWHM and amplitude of the SPR curves are considered simultaneously to optimize the performance of grating-based SPR sensor. According to our analysis, a set of optimized structural parameters are presented: $\Lambda=430\text{nm}$, $f=0.9$, $d=40\text{nm}$, $t=8\text{nm}$. A theoretical resolution of hydrogen concentration on the order of 0.001% is finally obtained in our design. Our study can provide instruction for fabricating highly sensitive grating-based SPR sensors and their application in hydrogen detection.

Acknowledgments

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