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Short Communication

Inverse surface plasmon resonance based effective hydrogen sensing using nanoscale palladium films

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ABSTRACT

We demonstrate a nanoscale palladium (Pd) based inverse surface plasmon resonance (ISPR) setup for sensing highly inflammable hydrogen (H_2) gas. The ISPR setup was employed in *Kretschmann* configuration to assess the sensitivity of the Pd-films when subjected to H_2 gas exposure. With an adequate broadening of the SPR peak maxima, the SPR angle was found to shift from a value of 46.57° to 50.97°, when the concentration of H_2 was varied between 0% and 0.9%. The shifting can be attributed to the transient development of isolated PdH_x ($x < 1$) clusters within Pd lattices, resulting in an appreciable change of refractive index locally. The dynamical behaviour of switching on/off states exhibited by a ~20 nm Pd-film and exposed to 0.1% H_2 gas was monitored over several cycles repetitively. The ISPR based H_2 sensor, as demonstrated in ambient environment, would find scope to detect low level H_2 in industrial and other hazardous areas.

1. Introduction

In recent decades, storing, recycling and sensing hydrogen (H_2) gas have received a great deal of attention not only by material science community but also by renewable energy specialists. The use of H_2 sensors is imperative while taking into account safety of life and property associated with H_2 gas production, mass storage and handling. The prospective applications can be realized in fuel cells, hydrogen-powered vehicles and hydrogenation reactions [1]. It is known, beyond doubt that, H_2 is highly inflammable in air, above a critical percentage of ~4% [2,3]. As a matter of fact, H_2 sensors have immense value for ensuing overall safety of both human beings as well as material resources. Moreover, accurate sensing of H_2 gas is extremely crucial while handling it locally. H_2 is primarily used as an alternative, clean energy source in advanced power plants [3]. In the past, numerous H_2 sensing devices have been tested and demonstrated. Nevertheless, low level detection of H_2 in ambient environment is still challenging as far as non-electrical probing is concerned. Previously, a number of optical methods were employed for H_2 sensing in Pd-films, to name a few, *Mach–Zehnder* interferometric fibre optic [4], extrinsic *Fabry–Perot* interferometric [5], micro-mirror [6] and fibre *Bragg* grating [7] sensors. Recently, sensing based on electrical measurements has been exploited using Pd nanoparticles [8].

Since the original work reported by Chadwick et al [9], surface plasmon resonance (SPR) based sensors have received considerable interest owing to measurement accuracy, cost effectiveness and easy handling. Undoubtedly, the work carried out by Chadwick and co-workers, owing to its novelty and originality, aroused a great deal of interest among the scientific community engaged in H_2 sensing devices. However, the sensing was carried out in vacuum and with a very high percentage (5%) of H_2 as the test gas. Earlier it was predicted that, 4% of H_2 in air is highly inflammable, and thus can be extremely risky. Keeping in mind safety considerations in the working area, we designed a setup which is capable of detecting very small amount of H_2 in ambient environment. Due to numerous advantages, the SPR based sensors have been tested for several applications, including bulk liquid measurement [10], gas detection [11], light modulation [12], refractive index measurement [13], thin film characterization [14], immuno-sensing [15] and DNA translocation [16]. The SPR mediated, Au–Pd nanocrystal based reusable sensor [1], as well as wavelength modulation based precision sensor [17] have been demonstrated very recently. While every method has its own advantage with regard to design consideration, operational ease, and data acquisition, yet scope for further improvement do exist that rely on SPR techniques.

Herein, we demonstrate an effective means of sensing low level H_2 gas by using a custom made setup based on inverse surface

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plasmon resonance (ISPR) in *Kretschmann* configuration [18,19]. The ISPR response was first discussed in 1993 [18], while the importance of ISPR could be extended to plasmonics as worked out by Zuccon et al. using functional Pd films [20]. In order to evaluate the sensitivity and switching on/off response, experiments were conducted on the nanoscale Pd films deposited on the hypotenuse face of a right angled prism (*BK7*, $n = 1.51$) and subjected to H_2 exposure.

2. Experimental: materials and methods

A schematic of the H_2-gas sensing set-up is shown in Fig. 1(a). Two right angled glass prisms (BK7), each having a dimension of 29 mm × 29 mm × 48 mm and having a refractive index (n) of 1.51, were placed at an angular separation of ∼5° and mounted on a circular, graduated prism table, having an angular resolution of ∼ 0.01°. As compared to the conventional single prism set-up, our sensing assembly offers two distinct advantages. First, the use of a high cost goniometer is not required in the present set-up and second, detector position can be fixed irrespective of different incident angles [21]. The next step was to prepare a gas mixing chamber and necessary gas flow arrangements with the help of which the sensing experiment could be undertaken easily (see supplement). It mainly comprise of two cylinders carrying H_2 (sensing gas) and N_2 (carrier gas) along with independent control valves and micro-flow controllers (MFC) so as to control the flow of gases through the mixing chamber (surrounding the prism table).

Prior to experiment, the hypotenuse face of the glass prism was coated with a ∼20 nm thick Pd-film by means of thermal evaporation technique (∼10^{-6} mbar) using a HIND HIVAC-12A4D vacuum coating unit. The Pd-coated prisms were then preserved in a vacuum dessicator to prevent environmental degradation and oxidation. A *p*-polarised light beam from a He–Ne red laser ($\lambda = 632.8$ nm, $P = 2$ mW) was first split into two perpendicular components by a 50:50 cube beam splitter, where one part (namely, reference beam), is directly coupled to a photodetector (PD_1). The straight beam was allowed to incident at one face, I_1 of the glass prism, as shown in Fig. 1(a). The beam underwent modulation and suffered total internal reflection at the hypotenuse face H_1 and subsequently, coupled to a second prism with the output light passing through E_2 and falling on a Si-photodetector (PD_2) which is sensitive in the red-infrared region of the electromagnetic spectrum. Consequently, light signal from both the reference and the modulated paths is fed to a custom-made instrumentation amplifier. In order to convert the amplified analog signal into a digital output, a 12-bit analog-to-digital converter (ADC) circuit was designed using an IC AD7875 and coupled to the output of the instrumentation amplifier. The digital output is monitored through a PC interfaced to the amplifier circuit. A software code has also been developed in *C* language for controlling the set-up and data acquisition. The rotation of the prism table was controlled via a gear-based stepper motor (precision ± 0.01°) using the developed code.

3. Theoretical treatment

Fig. 1(b) depicts thickness dependent ISPR curves of nanoscale Pd films deposited on the face H_1 of the right angle prism placed in the *Kretschmann* configuration. As can be found, there is an intimate relationship between the thickness of the Pd-films and sharpness of the ISPR peak located at∼46.57° which is close to the peak (∼46.72°) predicted by theoretical means (see supplement). The formula used for the reflection coefficient can be given by [22]:

$$r = \frac{(m_{11} + m_{12}q_3)q_1 - (m_{21} + m_{22}q_3)}{(m_{11} + m_{12}q_3)q_1 + (m_{21} + m_{22}q_3)} \quad (1)$$

Here, m_{xy} refers to individual matrix elements of M and $q = n_i \cos\theta$ [n_i is the refractive index of the ith layer with θ as the incident angle]. The characteristic reflectance, $R = |r^2|$. The sharpness of the ISPR peak was found to be maximum corresponding to a film thickness of ∼20 nm, as a much thicker film (∼100 nm) is likely to suppress the SPR features substantially, while an extremely thin film (<5 nm) would not result a prominent peak due to collective excitation of inadequate number of conduction electrons [23]. Along with a notable full width broadening, the characteristic reflectance is dropped by nearly 27% when the Pd film thickness was varied between ∼20 and 55 nm. The path of the light beam, while passing through various media (air to glass, glass to Pd film, etc.), is illustrated in the form of a ray diagram, highlighted in the inset of Fig. 1(b).

4. Results and discussion

The reflectance response of the film, which was measured as a function of angle of incidence, is substantially manifested when exposed to H_2 gas. As can be found from Fig. 2(a), the ISPR peak maxima exhibited a clear shifting toward a higher incidence angle with increasing H_2 concentration. The shifting was as large as ∼4.4° when the concentration of H_2 was varied between 0% and 0.9%. While ISPR peaks retained the symmetry, an apparent increase in the full width half maxima (FWHM) could be realized when the film was exposed to a higher concentration of H_2. The

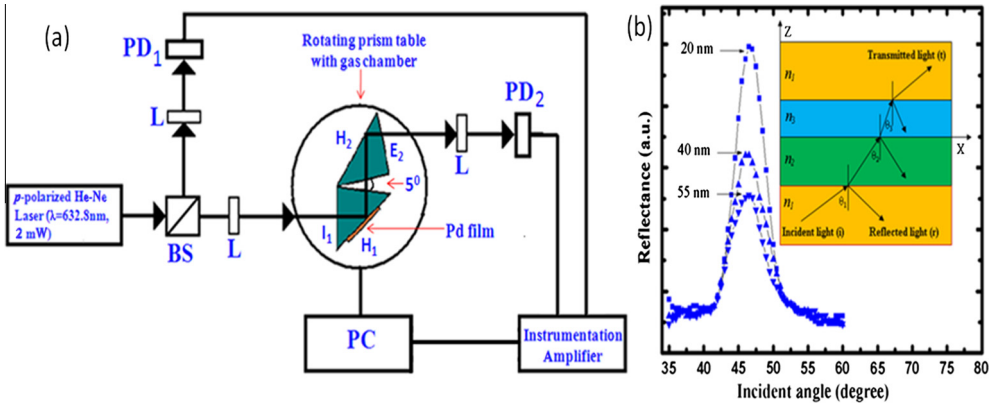

Fig. 1. (a) The schematic diagram of experimental setup for sensing H_2 gas. The symbols BS, L, PD and PC basically represent beam splitter (BS:50:50), plano-convex lens, photodetector and personal computer; respectively. The Pd film thickness (20 nm, 40 nm and 55 nm) dependent ISPR responses along with schematic ray diagram (not to scale) is shown in (b). In the scheme, air, glass (right angle prism) and Pd thin film media are characterized by refractive indices n_1, n_2 and n_3; respectively.