Effect of Calcium Fluoride Buffer on PdY deposited Optical Fiber Hydrogen Sensor

Mukesh Pratap Singh¹ and Santosh Kumar Chaurasia²

¹ Faculty of Engineering & Technology, Jamia Millia Islamia, New Delhi
² ABES Engineering College, Ghaziabad, Uttar Pradesh, India

Email: Santosh.chaurasia@abes.ac.in

Abstract. Optical fiber sensor having transducer layer PdY is highly sensitive to detect hydrogen. The main advantage of PdY is reducing the cracking effect in optical fiber hydrogen sensor having transducer thickness palladium. To analyze the optical fiber H₂ sensor apply the modal approach. The effect of calcium fluoride buffer influencing the optical fiber hydrogen sensor of sensitivity. The thickness of calcium fluoride buffer and palladium yttrium alloy layers are maximized to obtain higher sensitivity.

Keywords — Calcium fluoride Buffer, Fiber Hydrogen detection, Polished optical fiber, PdY.

1. Introduction
The catastrophic problem in our living world is pollution. Various causes of pollution, such as emission of different chemicals and gases from industry and vehicles. To reduce the pollution happen due to combustion of fuels in vehicles are reduced by using eco friendly fuel. Hydrogen is the one of the alternate energy source which is eco friendly and it application as a fuel [1][2]. At the flammability range is 4.0-74.5% of hydrogen, which is explosive. [3]. Due to this necessity its sensing is important when it is transported, storage and in use[4]. Semiconductor hydrogen sensors are already discussed [5]. Semiconductor hydrogen sensors are having the drawbacks such as produces explosion if leaking of hydrogen happen. To overcome this drawback fiber sensors are preferred to detect hydrogen. fiber sensor large number of advantages [6]. Different types of optical fiber hydrogen sensors are reported in literature and most of them are based on the interaction of the evanescent field with hydrogen through a transducer [7-9]. The detection of hydrogen having sensing layer is metallic. Then various modes supported at the interface of sensing and buffer layer [10]. One of the phenomenon surface Plasmon resonance happen at these interface. [11-12]. An Surface Plasmon resonance (SPR) is generated by coupling between an evanescent wave and Plasmon[13]. The palladium based optical fiber sensor is highly sensitiy but its disadvantage is that these sensors are damaging due to cracking of the Pd lattice which occurs during repeated hydrogen loading cycles [14–16]. More recently, Tabassum et al investigated the use of a nanocomposite of Pd nanoparticles in a host matrix of ZnO [17]. The sensor demonstrated excellent performance however cross-sensitivity to gases other than hydrogen was reported. Another method of circumventing the problem of mechanical damage to Pd during hydrogen sensing is to alloy it with other metals. Sengar et al have shown that when inducing of hydrogen producing the distortion effects on palladium ,By alloying palladium with gold and palladium with copper, these effects may be minimized[18]. Zhao et al have investigated the use of a Pd–Au film and shown that the α to β phase transition is suppressed in this alloy [19]. Liu et al have
shown that, by alloying a Pd film with Y, mechanical stress on the Pd lattice is significantly reduced [20]. To detect hydrogen with reduced cracking effect PdY is highly reliable.

2. Numerical Procedure

Optical fiber hydrogen sensor as a schematically view shown in fig.1. To simulate numerically optical fiber hydrogen sensor is represented in planar structure. [23]. The planar structure of optical fiber hydrogen sensor is shown in fig.2. This fig. Shows that the planar structure of optical fiber hydrogen sensor having three regions which is defined as input regions, sensing regions and output regions.

Numerical simulations have performed on planar structure of optical fiber hydrogen sensor having calcium fluoride (CaF$_2$) buffer and transducer PdY. And effective index and TM fields corresponding to each regions, such as input regions, sensing region and output region, had done. [21]. At the interface of input regions and sensing regions, sensing regions and output regions obtained excitation coefficients and optical output optical power presence and absence of hydrogen[22]. Permittivity of palladium yttrium alloy affected when it absorb the hydrogen. The effect of this field in sensing region changes. Then excitation coefficient is also affected then optical output power changes. When hydrogen is adsorbed in palladium yttrium layer output optical power increases. All the simulations have done at a wavelength 1550 nm.
In order to mitigate $\alpha$ to $\beta$ phase change that normally accompanies hydrogen absorption, the thin film of Pd was alloyed with Y. When this happen the lifespan of this OFC H$_2$ sensor increases. Permittivity of Y [24-25],

$$\varepsilon_Y = 2 - \frac{\omega_p^2}{\omega^2 - i\omega\gamma_{fc}} + \frac{S_{IB}\omega_p^2}{(\omega_{IB}^2 - \omega^2 - i\omega\gamma_{IB})}$$

Due to this complex permittivity of pure palladium changes and then complex permittivity of palladium reduces. The permittivity of Palladium hydride is specified by mathematical formulation. Where $\varepsilon_{pd}(0)$ is permittivity in presence of pure nitrogen [29]. When 4% H$_2$, $h$ is equal to 0.8 [26,30]. Effective permittivity of two metal is represented [27,28]. where $f_1$ is10 %. 

$$E_{\text{effective}} = f_1E_1 + (1 - f_1)E_2$$

The important parameter sensitivity is equal to the 10log10(output optical power in hydrogen gas/output optical power without hydrogen gas).

3. Results and Discussions
Calcium fluoride index is 1.426 [31]. In fig.3 optical fiber hydrogen sensor sensitivity (S) changes with respect to calcium fluoride buffer thickness (ba) at a 30 nm fixed transducer PdY thickness(ta),. From the fig. Observed that maximum sensitivity appear at a calcium fluoride buffer thickness 0.51 $\mu$m and with increase or decrease thickness of calcium fluoride i.e. higher or lower thickness from 0.51 $\mu$m, sensitivity is decreasing in nature.

```
Variation between transducer PdY thickness(ta) and sensitivity is represented in fig.4. With increasing transducer thickness(ta), sensitivity increases and a optimum sensitivity achieved at a certain thickness of transducer ,and after a certain transducer thickness sensitivity decreases, with again increase of transducer PdY thickness ,sensitivity become saturate. The effect of absorption of hydrogen in PdY
```

![Fig.3: Sensitivity of optical fiber hydrogen varies with respect to calcium fluoride thickness(ba) at a 30 nm transducer thickness(ta).](image-url)
Fig. 4: The sensitivity ($S$) of the optical fiber hydrogen sensor with respect to PdY thickness ($t_m$) for calcium fluoride thicknesses ($b_m$) = 0.1 µm ( ), 0.2 µm ( ), 0.3 µm ( ), 0.5 µm ( ).

Fig. 5: Sensitivity of optical fiber hydrogen sensor with respect to optimum calcium fluoride thickness ($b_a$) corresponding to PdY thicknesses $t_a$ = 5 nm ( ), 10 nm ( ), 20 nm ( ), 30 nm ( ), 40 nm ( ), 50.01 nm ( ).
region, change in happen its permittivity, due to this effective index is changes which changes the output optical power. At a optimum calcium fluoride thickness ($b_{\text{optimum}}$) and sensing layer thickness ($t_{a_{\text{optimum}}}$) 50.01, sensitivity maximizes.

The sensitivity of optical fiber hydrogen sensor changes with respect to calcium fluoride thickness as a various transducer layer thickness, which is shown in fig. 5. From the fig. observed that when the calcium fluoride thickness increases sensitivity increases and after a certain thickness sensitivity decreases.

Fig. 6: The optimum calcium fluoride thickness ($b_{a}$) of the optical fiber hydrogen sensor varies with respect to sensing layer thickness ($t_{a}$).

Fig. 7: Sensitivity versus hydrogen concentration (ppm) in which the thickness values of calcium fluoride thickness $b_{a}=1.0 \ \mu m$ and sensing area PdY thickness $t_{a}=30 \ \text{nm}$ ($\times$) optimum calcium fluoride thicknesses $b_{a}=0.51 \ \mu m$ and optimum transducer thickness 50.01 nm ($\circ$).
Fig. 6. shows that variation of the calcium fluoride optimum buffer thickness with the transducer (palladium yttrium alloy) thickness. Here seen that when the palladium yttrium alloy thickness becomes smaller, optima of calcium fluoride buffer thickness becomes higher and when the palladium yttrium thickness becomes higher the saturation of optima of calcium fluoride thickness occurred. On the basis of results of figure.6 a relation is developed between calcium fluoride (b_{opt}) and PdY(ta) thickness.

\[ b_{opt} = -A_{ap} t_{a}^{6} + B_{ap} t_{a}^{5} - C_{ap} t_{a}^{4} + D_{ap} t_{a}^{3} - E_{ap} t_{a}^{2} + F_{ap} t_{a} - G_{ap} \]

Where \( A_{ap}, B_{ap}, C_{ap}, D_{ap}, E_{ap}, F_{ap}, G_{ap} \) are coefficients and values are \( A_{ap} = 2.2 \times 10^{-12}, B_{ap} = 1.1 \times 10^{-10}, C_{ap} = 2.2 \times 10^{-7}, D_{ap} = 2.3 \times 10^{-5}, E_{ap} = 0.0014, F_{ap} = 0.051 \) and \( G_{ap} = 0.22 \).

We have plotted sensitivity (S) with respect to different percentage of hydrogen is shown in Fig. 7. and we observed that with increasing in hydrogen percentage, S also increases and its nature is linear. When we use optimum Calcium fluoride buffer thickness and transducer thickness then found that nearly 6.5 dB improvement in sensitivity when hydrogen concentration is 4%.

![Fig.8: Sensitivity versus length of sensor for the calcium fluoride thickness b_{a}=1.0 \mu m and PdY sensing thickness t_{a}=30 nm ( ) calcium fluoride optimum thicknesses b_{a}=0.51 \mu m and transducer thickness optimum thickness 50.01 nm ( )](attachment:Fig8.png)

We have plotted the sensitivity (S) with respect to sensing length is shown in Fig. 8. and we observed that with increase in sensor length sensitivity also increases and its nature is linear. When we use optimum Calcium fluoride buffer thickness and transducer thickness then found that nearly 6.5 improvement in sensitivity [32].

4. Conclusions

Optical fiber with clad buffer and transducer PdY alloy layer numerically investigated. The main outcomes of this study is to optimize the calcium fluoride buffer thickness and sensing layer thickness to achieve the high sensitivity and the sensing layer PdY in which the role yttrium is to reduce the blistering effect of hydrogen sensor. Coupling of guided modes and Plasmon modes are controlled by calcium fluoride buffer which is present core of the fiber and transducer PdY layer. And optimize palladium yttrium and clad buffer provides the higher sensitivity. Then 6.5 dB higher sensitivity achieved.
References

[1] Robert S. Cherry 2004 A hydrogen utopia? Int. J. of Hydrogen Energy, vol. 29, pp. 125-129.
[2] R. Ramachandran and R. K. Menon 1998 An overview of industrial uses of hydrogen, Int. J. of Hydrogen Energy, vol. 23, pp. 593-598.
[3] D. A. Crowl and Y. Go 2007 The hazards and risks of hydrogen J. of Loss Prevention in the Process Industries, vol. 20, pp. 158-164.
[4] T. H’ubert, L. Boon-Brett, V. Palmisano, and M. A. Bader 2014 Developments in gas sensor technology for hydrogen safety Int. J. of Hydrogen Energy, vol. 39, pp. 20474-20483.
[5] C. Christofides and A. Mandelis 1990 Solid-state sensor for trace hydrogen gas detection J. Appl. Phys. vol. 68, no.6, R1-R30.
[6] G. Orellana and D. Haigh 2008 New trends in fiber-optic chemical and biological sensors Current Analytical Chemistry, 2008, vol. 4, pp. 273-295.
[7] M. Tabib-Azar, B. Sutapun, R. Petrick, and A. Kazemi 1999 Highly sensitive hydrogen sensors using palladium coated fiber optics with exposed cores and evanescent field interactions,” Sens. Actuators B, vol. 56, no.1–2, pp. 158–163.
[8] J. Villatoro, A. Diez, J. L. Cruz, and M. V. Andrés 2001 Highly sensitive optical hydrogen sensor using circular Pd-coated single-mode tapered fiber Electron. Lett., vol. 37, no. 16, pp. 1011–1012.
[9] D. Zalvidea, A. Diez, J. L. Cruz, and M. V. Andrés 2006 Hydrogen sensor based on a palladium-coated fibre-taper with improved time response Sens. Actuators B, vol. 114, no. 1, pp. 268–274.
[10] F. Yang and J. R. Sambles 1997 Determination of the optical permittivity and thickness of absorbing films using long range modes J. Mod. Opt., vol. 44, pp. 1155–1163.
[11] P. Bhatia and B. D. Gupta 2012 Surface plasmon resonance based fiber optic hydrogen sensor utilizing wavelength interrogation Proc. of SPIE, vol.8351, pp. 83511V-1-6.
[12] Rana Tabassum and Banshi D. Gupta 2015 Surface plasmon resonance-based fiber-optic hydrogen gas sensor utilizing palladium supported zinc oxide multilayers and their nanocomposite Applied Optics vol. 54, no. 5 pp.1032-1040.
[13] J. Homola 2006 Surface Plasmon Resonance Based Sensors. New York:Springer.
[14] Armgarth M and Nylander C 1982 Blister formation in Pd gate MIS hydrogen sensors IEEE Electron Device Lett.3 384–6.
[15] Choi S Y, Takahashi K, Esashi M and Matsuo T 1986 Stabilization of MISFET hydrogen sensors Sensors Actuators B 9 353–61.
[16] Mandelis A and Garcia J A 1998 Pd/PVDF thin film hydrogen sensor based on laser-amplitude-modulated opticaltransmittance:dependence on H-2 concentration and device physics Sensors Actuators B 49 258–67.
[17] Tabassum R and Gupta B D 2016 Fiber optic hydrogen gas sensor utilizing surface plasmon resonance and native defects of zinc oxide by palladium J. Opt. 18 015004.
[18] Sengar S K, Mehta B R, Kuliриya P K and Khan S A 2013 Enhanced hydrogenation and reduced lattice distortion in size selected Pd–Ag and Pd–Cu alloy nanoparticles Appl. Phys. Lett. 103 173107.
[19] Zhao Z, Carpenter M A, Xia H and Welch D 2006 All-optical hydrogen sensor based on a high alloy content palladium thin film Sensors Actuators B 113 532–8.
[20] Liu Y, Chen Y P, Song H and Zhang G 2013 Characteristics of an optical fiber hydrogen gas sensor based on a palladium and yttrium alloy thin film IEEE Sens. J. 13 2699–704.
[21] E. K. Sharma and M. P. Singh 1993 Multilayer waveguide devices with absorbing layers J. of Optical Communications, vol. 14, pp. 134-137.
[22] M P. Singh and A. Sharma 1998 Wavelength selectivity of in-line fiber optic filter devices Applied Optics, vol. 37, no. 27, pp. 6350-6354.
[23] A. Sharma, J. Kompella, and P. K. Mishra 1990 Analysis of fiber directional coupler and
coupler half-block using a new simple model for singlemode fibers J. of Lightwave Technol., vol. 8, no. 2, pp. 143-151.

[24] Weaver J H and Olson C G 1977 Optical-absorption of HCP yttrium Phys. Rev. B 15 590–4.

[25] Quinten M 2011 Optical Properties of Nanoparticle Systems (Weinheim: Wiley).

[26] X. Béevenot, A. Trouillet, C. Veillas, H. Gagnaire, and M. Clément 2002 Surface plasmon resonance hydrogen sensor using an optical fibre Meas. Sci. Technol., vol. 13, pp. 118-124.

[27] Sharma A K and Mohr G J 2008 On the performance of surface plasmon resonance based fibre optic sensor with different bimetallic nanoparticle alloy combinations J. Phys. D: Appl. Phys. 41 1–7.

[28] Sharma, Anuj K., and B. D. Gupta 2007 On the performance of different bimetallic combinations in surface plasmon resonance based fiber optic sensors Journal of applied physics 101.9: 093111.

[29] Ordal, M. A., Long, L. L., Bell, R. J., Bell, S. E., Bell, R. R., Alexander, R. W., & Ward, C. A. 1983 Optical properties of the metals al, co, cu, au, fe, pb, ni, pd, pt, ag, ti, and w in the infrared and far infrared. Applied optics, 22(7), 1099-1119.

[30] M. J. Dodge 1984 Refractive properties of magnesium fluoride, Appl. Opt., vol. 23, no. 12, pp. 1980-1985.

[31] Malitson, Irving H. 1963 A redetermination of some optical properties of calcium fluoride. Applied Optics 2.11 : 1103-1107.

[32] K. T. Kim, H. S. Song, J. P. Mah, K. B. Hong, K. Im, S. Baik, and Y. Yoon 2007 Hydrogen sensor based on palladium coated side-polished single-mode fiber,'IEEE Sensors Journal, vol. 7, no. 12, pp. 1767-1771.