Optical Fibre Surface Plasmon Resonance Sensor Based on a Palladium-Yttrium Alloy

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Abstract

This work investigates the use of a Pd alloy as the hydrogen sensitive layer in an optical fibre surface plasmon resonance hydrogen sensor. The performance of the sensor is modelled using the transfer matrix model for a multi-layered structure. The structure consists of an Ag/SiO₂/PdY stack deposited on the core of a multimode optical fibre. We detail the behaviour of the sensor in the spectral domain by investigating its sensitivity and detection accuracy. We find that careful choice of the Ag layer thickness is needed to optimise sensor performance.

1. Introduction

Hydrogen has excellent future potential as a clean renewable energy source, however due to its explosive nature, the development of robust hydrogen sensors is essential in order to facilitate its adoption [1]. Palladium-based sensors have found significant application to hydrogen sensing [2, 3] but lack durability due to blistering, cracking and delamination of the Pd surface which occurs during repeated hydrogen loading cycles [4-6]. Recently, Liu et al. have demonstrated that alloying Pd with Y can significantly reduce the mechanical stress on the sensor and prolong its lifetime [7, 8]. The sensor demonstrated by Liu et al. involved a thin PdY film which was interrogated optically via an optical fibre bundle. It was shown that the presence of hydrogen caused a measurable change in reflectance from the film. However the setup required the employment of a reference cell along with the sensing cell which significantly increases the footprint of the device. Additionally, the nature of the setup necessitated the use of...
relatively thick alloy film, which was shown to have a detrimental effect on sensor response time.

Fig. 1. (a) Optical configuration for the sensor; (b) Multi-layered structure of the sensor.

Optical fibre SPR sensors (OFSPR) have attracted significant interest for application to hydrogen sensing due to their ability to be remotely deployed in potentially explosive environments. Perrotton et al. have demonstrated a sensitive OFSPR sensor with a fast response time (<15s) which used Pd as the hydrogen sensitive layer [9]. However such a sensor is prone to mechanical wear during hydrogen loading as previously described. Recently, Wang et al. have proposed a sensitive OFSPR sensor which utilises a 4 layer sensing stack consisting of Ag/SiO2/WO3/Pt [10]. The sensor has better sensitivity than Perrotton’s however no information was provided on the durability or response time.

In this work we propose a sensor based on Ag/SiO2/PdY stack deposited on the core of a multimode optical fibre. The sensor has a similar fast response time to that of Perrotton but with improved durability derived from the Y content of the alloy. We discuss the design and operation of the sensor and in particular the factors which modulate its sensitivity and detection accuracy. The role of the different layers within the stack is discussed and a figure of merit is introduced which allows optimisation of sensor performance.

2. Theory

Using the transfer matrix formalism, the light intensity passing through the fibre at a particular wavelength can be written as [11]:

$$I_{out,\lambda} = \frac{1}{2} \int_{\theta_c}^{\theta_0} r_p(\theta)^{2N} I_{0,\lambda}(\theta_{in}) d\theta + \frac{1}{2} \int_{\theta_c}^{\theta_0} r_s(\theta)^{2N} I_{0,\lambda}(\theta_{in}) d\theta$$  \hspace{1cm} (1)

Where $r_p$ and $r_s$ are the reflection coefficients for incident TM and TE polarized radiation propagating through the fibre, $\theta$ is the propagation angle of rays within the fibre, $N$ is the number of fibre reflections that occur through the sensing region, and $\theta_c$ is the critical angle for ray guiding within the fibre [12]. Dielectric permittivity of the layers is modelled using the Brendel Bormann model for Ag and Pd [13], the Drude-Lorentz model for Y [14], and the Sellmeier formula for SiO2 [15]. For the permittivity of Pd hydride we use the experimental data obtained by von Rottkay et al. [16]. Finally, the average dielectric permittivity of the $Pd_xY_{1-x}$ alloy, $\varepsilon_A$, is assumed to vary with the composition average of the alloy [17].

$$\varepsilon_A(x, \lambda) = x\varepsilon_{Pd}(\lambda) + (1 - x)\varepsilon_{Y}(\lambda)$$  \hspace{1cm} (2)

3. Results and Discussion

We investigate a sensor utilising a $Pd_{0.9}Y_{0.1}$ alloy with a sensing length $L$ of 1cm, fibre diameter of 200μm and NA of 0.22. The alloy layer thickness was fixed at 3nm in order to ensure a fast sensor response time as well as maintaining ease of fabrication [7]. Sensitivity is defined in the usual way [18] and detection accuracy (DA) is defined in Equation 3, where the inverse of the spectral difference between two points 10% above the minimum
The intensity of the hydride curve is denoted $\Delta \lambda_{10}$ [15].

$$DA = \frac{1}{\Delta \lambda_{10}}$$  \hspace{1cm} (3)

Fig. 2. (a) The transmitted intensity through the fibre sensor for a multi-layer sensing structure of Ag ($d_1=30\text{nm, } 40\text{nm, } 50\text{nm}$) / SiO$_2$ ($d_2=180\text{nm}$) / PdY ($d_3=3\text{nm}$). In the presence of hydrogen the SPR dip undergoes a red shift; (b) Effect of Ag layer thickness ($d_1$) on sensor sensitivity with SiO$_2$ ($d_2=100\text{nm, } 140\text{nm, } 180\text{nm}$) / PdY ($d_3=3\text{nm}$).

In Figure 2(a), we demonstrate the effect of varying the Ag layer thickness ($d_1$). We find that increasing $d_1$ causes a red shift in the resonance wavelength as well as a decrease in the depth of the SPR dip which in turn can be expected to degrade the DA. Figure 2(b) displays the sensor sensitivity for varying Ag and SiO$_2$ thicknesses ($d_2$). We include the effect of $d_2$ here as it influences the spectral centre of the SPR dip and therefore can be used to align this with the spectral centre of the light source [12]. In Figure 2(b), we see the general trend that increasing $d_1$ improves sensitivity. We find that structures with a thinner SiO$_2$ layer have better sensitivity. In practice, there is a lower limit on the SiO$_2$ layer thickness as decreasing it too much pushes the resonance into the UV which would be impractical for most purposes.

Fig. 3. (a) Detection Accuracy; (b) Sensor Figure of Merit for a multi-layer sensing structure of SiO$_2$ ($d_2=100\text{nm, } 140\text{nm, } 180\text{nm}$) / PdY($d_3=3\text{nm}$).

Figure 3(a) shows that the DA demonstrates a fairly flat behaviour over a wide range of Ag thicknesses ($d_1$) before falling off at the higher end. This can be understood as the effect of the degradation in the depth of SPR dip at higher values of $d_1$ as shown in Figure 2(a). Figures 2(b) & 3(a) together show that a trade-off between sensitivity and DA is required for an optimum sensor. To this end, we define a figure of merit (FOM) which allows us to determine the optimal sensing structure [15].
\[ FOM = \frac{\Delta \lambda_{res}}{\Delta C} \]  

Where, \( \Delta C \) is the change in hydrogen concentration the sensor is exposed to. In Figure 3(b), the FOM for the sensor is plotted. The peak in each curve represents the optimum sensing point for each of the 3 sensors. We can see that, for each of the 3 structures examined, there is a specific Ag thickness which gives the best sensor performance.

4. Conclusion

We have outlined the performance of an Ag/SiO\(_2\)/PdY multilayer OFSPR sensor. We find that decreasing the thickness of the SiO\(_2\) layer increases the sensitivity of the sensor but has little effect on its DA. The Ag thickness affects the spectral location and depth of the SPR and we find that the optimal Ag thickness depends on the width of SiO\(_2\) and PdY layers. FOM calculations demonstrate the optimal Ag thickness corresponding to each of 3 different simulated SiO\(_2\) thicknesses. For a sensor with SiO\(_2\) and PdY layers of 100nm and 3nm, the optimum Ag thickness is 48nm and the presence of 1% hydrogen shifts the resonance wavelength by 4.3nm.

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References