

Surface Plasmon Generation in a Subwavelength Slit in metal: a Palladium-Based H_2 Leak Detection Sensor

M.A. Vincenti^{1,2}, D. de Ceglia², M. De Sario¹, V. Marrocco¹, V. Petruzzelli¹,
F. Prudenzano³, M. Scalora², and A. D'Orazio¹

¹Dipartimento di Elettrotecnica ed Elettronica, Politecnico di Bari, Via Orabona 4 – 70125, Bari - Italy
vincenti@deemail.poliba.it

² Charles M. Bowden Research Center, AMSRD-AMR-WS-ST, Redstone Arsenal, AL 35898-5000, USA

³ Dipartimento di Ingegneria dell'Ambiente e per lo Sviluppo Sostenibile, Politecnico di Bari, Taranto, Via del Turismo 8, 74100, Italy

Abstract. *We investigated the extraordinary transmission that occurs for subwavelength slits on metallic substrates: the transmission process is driven by several physical mechanisms, whose relative importance depends on the thickness of the metallic substrate and slit size. We show how a Palladium-based device is suitable for H_2 -leak-detection exploiting the enhanced transmission phenomenon.*

Introduction

The demand for using hydrogen as a next-generation, clean, and renewable energy source has stimulated considerable efforts toward developing sensitive, reliable, and cost-effective hydrogen sensors for the fast detection of hydrogen below the lower explosive limit (LEL) of 4.65% [1]. Currently, Pd or Pd-based alloys are commonly used as sensing material, due to palladium high sensitivity and selectivity toward hydrogen [2-4]. Manipulation and storage of hydrogen are associated with danger of leakage which leads to an explosive atmosphere if the hydrogen concentration exceeds the LEL. Therefore, the development of sensors for hydrogen detection is important to preserve human beings and equipments. The literature reports several examples of hydrogen sensors based on chemical or electronic approaches [5-9]. Chemical hydrogen sensors measure changes induced by reaction between hydrogen and a corresponding chemical transducer, such as palladium [10-12]. Moreover, optical sensors are highly important for use in dangerous environment where explosive concentration of hydrogen could occur. The detection of very small quantities of hydrogen in the surrounding environment can be operated by monitoring the transmitted field of a subwavelength slit carved on a palladium substrate: the association of resonance cavity effects and surface plasmon generation allows the investigation of a regime of extraordinary transmittance in which the sensitivity to the variation of the optical properties is dramatically increased due to the presence of surface waves inside the nanocavities.

Transmission From a Single Slit

Several theoretical and experimental works report on the ability of subwavelength apertures carved on metal substrates to enhance the transmitted field thanks to the coupling of surface plasmons inside the nanocavities [13-15]. In this paper we investigate the enhanced transmission phenomenon that occurs for a single slit carved on an opaque metal substrate by inspecting two different mechanisms, respectively

driven by two different geometrical parameters: the thickness of the metallic substrate and the aperture size. The device under investigation is depicted in Fig.1-a : it consists of a palladium layer whose key parameters are the metal thickness w and the slit size a . All the calculations and results reported below are obtained solving Maxwell's equations by means of a proprietary numerical code based on a full-wave, finite-difference, time-domain method (FDTD) [16] and considering a Gaussian shaped incident input tuned at 800nm. Dispersion and absorption of the Palladium layer are considered in all the simulations [17]. Fig.1-b shows the transmission coefficient obtained by changing the metal thickness w and the slit size a by considering the source input described above and normalizing the transmitted field to the energy that only impinges the slit: the Fabry-Perot-like behavior of such structures is altered respect to previously reported transmittance peculiarities of equivalent perfect electric conductor structure [18], meaning that the presence of a plasmon resonance inside the nanocavity plays a fundamental role in the resonant mechanism as well as in the enhanced transmission phenomenon, resulting in the enhancement of the transmitted field due to the double coupling between the resonant conditions that depend on the metal thickness and on the slit size.

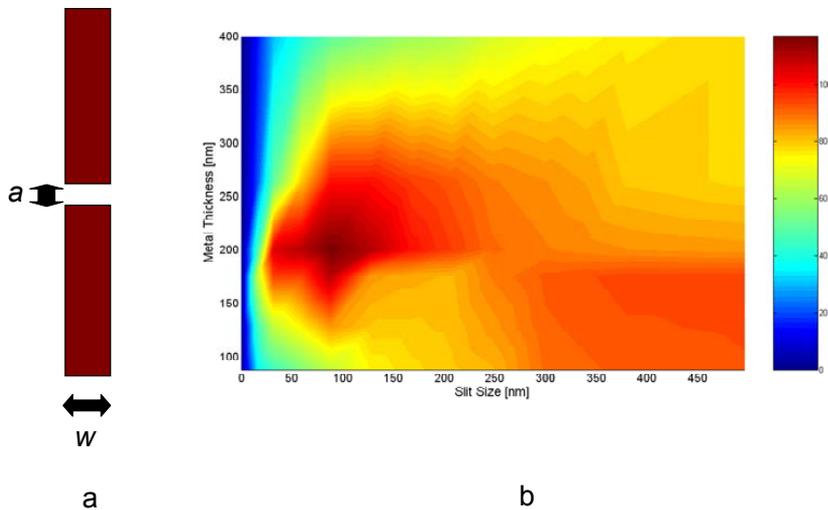


Fig.1: a) Sketch of the palladium substrate: the parameters under investigation are a (slit size) and w (substrate thickness) b) Transmission coefficient evaluated by varying the metal thickness w and the aperture size a ; The presence of a resonance located for $w=200\text{nm}$ confirms the Fabry-Perot like behavior of the structure.

The Palladium-Based Sensor: operating principle

As it is well known, the majority of transition metals spontaneously absorb hydrogen, changing their mechanical and optical properties as a function of the hydrogen content in the environment. Palladium, indeed, shows an extraordinary ability of trapping hydrogen molecules in its electrical configuration free states, modifying its Fermi level and changing reversibly its electrical [10] and optical [11] properties. This phenomenon causes the decrease of both the real and the imaginary parts of the complex permittivity

of palladium [17] described by means of a simple function h , that relates the bare palladium permittivity to the hydride palladium one as follows:

$$\varepsilon_{PdH}(\omega) = h(\omega) \times \varepsilon_{Pd}(\omega) \quad (1)$$

where $\varepsilon_{Pd}(\omega)$ is the dielectric permittivity of bare Pd, $\varepsilon_{PdH}(\omega)$ is the dielectric permittivity of hydride Pd, and $h(\omega)$ is a nonlinearly decreasing function that assumes real values between 1 and 0 by increasing the hydrogen concentration [19]. Moreover, to take into account the dispersive properties of both bare and hydride palladium, we consider the Drude model, which remains valid by increasing the hydrogen concentration inside the Pd lattice [6,7,12]. As mentioned in the previous section the peak in the transmission coefficient for a carved metal substrate corresponds to a perfect coupling condition inside the subwavelength aperture, meaning that also a slight variation in the optical properties of the palladium induces a dramatic change in the coupling phenomenon and, as a consequence, in the transmitted field. As depicted in Fig.2 the variation associated to the increase of the hydrogen content in air is remarkable: the sensitivity of the sensor calculated as the ratio between the variation of the transmission coefficient over the hydrogen content variation [6], is equal to $S=0.567 \text{ \%}\cdot\text{ppm}^{-1}$ when the hydrogen content goes from 0ppm to 100ppm.

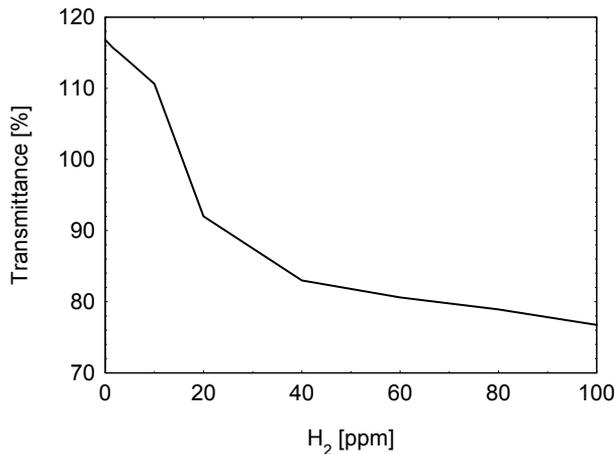


Fig2: Sensor calibration curve: transmittance value decreases as a nonlinear function of the hydrogen content, showing a sensitivity $S=0.567 \text{ \%}\cdot\text{ppm}^{-1}$ when the hydrogen content goes from 0ppm to 100ppm.

Conclusions

We theoretically investigated on the extraordinary transmission phenomenon that occurs for sub-wavelength slits carved on opaque metal substrates, i.e. palladium. Due to the dramatic response of palladium to hydrogen presence and to the combination of cavity effects and surface waves inside the slit one can explore the quantity of this gas by simply monitoring the changes in the transmitted field.

Acknowledgments

M.A. Vincenti thanks the U.S. Army European Research Office for partial financial support (contract no. W911NF-07-1-0567).

References

- [1] F.A. Lewis, "The Palladium Hydrogen system", New York: Academic, 1967.
- [2] P.T. Moseley, J.O.W. Norris and D.E. Williams, "Techniques and Mechanism in gas sensing", Philadelphia, PA: IOP, 1991.
- [3] K. Hara and N. Nishida, "H₂ sensor using Fe₂O₃ based thin film", Sens. and Actuators B, vol. 20, pp. 181, 1994.
- [4] S. Basu and A. Dutta, "Modified heterojunction based on zinc oxide thin film for hydrogen gas sensor application", Sens. and Actuators B, vol. 22, pp. 83-87, 1994.
- [5] M.A. Vincenti, S. Trevisi, D. de Ceglia, N. Cioffi, M. Scalora, M. De Sario, V. Petruzzelli, F. Prudenzano, A. D'Orazio, "Metallo-Dielectric Multilayer Sensor for Hydrogen Detection in Exhaled Breath", ECIO 2007 - 13th European Conference on Integrated Optics, Copenhagen Denmark, 25-27 April 2007, paper ThG12.
- [6] M.A. Vincenti, A. D'Orazio, M. De Sario, V. Petruzzelli, F. Prudenzano, D. de Ceglia, M. Scalora, "Fabry-Perot Microcavity Sensor for H₂-Breath-Test Analysis", Jour. of Appl. Phys. vol.102, no.7 074501, 2007.
- [7] M.A. Vincenti, S. Trevisi, M. De Sario, V. Petruzzelli, A. D'Orazio, F. Prudenzano, N. Cioffi, D. de Ceglia, M. Scalora, "Theoretical Analysis of a Novel Palladium-Based Metallo-Dielectric Photonic Band Gap Structure for Applications to H₂ sensors", Jour. of Appl. Phys. vol. 103, no. 4, 2008.
- [8] V.R. Katti, A. K. Debnath, S.C. Gadkari, S.K. Gupta, and V.C. Sahni, "Passivated thick film catalytic type H₂ sensor operating at low temperature", Sens. and Actuators B, vol. 84, pp. 219-225, 2002.
- [9] K. Domansky, A. Rose, W.H. Grover, and G. J. Exharos, "Localized deposition of zinc oxide films by automated fluid dispensing method", Mater. Sci.Eng. B, vol.76, no.2, pp. 116-121, 2000.
- [10] J.C. Barton, J.A.S. Green, F.A. Lewis, "Changes of electrode potential and electrical resistance as a function of the hydrogen content of some Pd + Ni and Pd + Rh alloys", Trans. Faraday Soc., vol.62, pp. 960-970, 1966.
- [11] A. Mandelis, J.A. Garcia, "Pd/PVDF thin film hydrogen sensor based on laser amplitude modulated optical transmittance: dependence on H₂ concentration and device physics", Sens. Actuators B, vol. 49, pp. 258-267, 1998.
- [12] K. Wyrzykowski, A. Rodzik, B. Baranowski, "Optical transmission and reflection of PdH_x thin films", J. Phys. Condens. Matter, vol. 1, pp. 2269-2982, 1999.
- [13] T.W. Ebessen, H.J. Lezec, H.F. Ghaemi, T. Thio and P. A. Wolff, "Extraordinary optical transmission through subwavelength hole arrays", Nature 391, 667-669, 1998.
- [14] J. Bravo-Abad, L. Martin-Moreno and F.J. Garcia-Vidal, "Transmission properties of a single metallic slit: from the subwavelength regime to the geometrical optical limit, Phys. Rev. E 69, 026601, 2004.
- [15] R. Gordon, "Light in a subwavelength slit in metal: propagation and reflection", Phys. Rev. B 73, 153405, 2006.
- [16] R.W. Ziolkowski, "Pulsed and CW Gaussian beam interactions with double negative metamaterials slab", Opt. Express 11, 662, 2003.
- [17] M.A. Ordal, L.L. Long, R.J. Bell, S.E. Bell, R.R. Bell, R.W. Alexander, C.A. Ward, "Optical properties of the metals Al, Co, Cu, Au, Fe, Pb, Ni, Pd, Pt, Ag, Ti, and W in the infrared and far infrared", Appl. Optics 22, 1099-1120, 1983.
- [18] T.W. Ebessen, H.J. Lezec, H.F. Ghaemi, T. Thio and P. A. Wolff, "Extraordinary optical transmission through subwavelength hole arrays", Nature 391, 667-669, 1998.
- [19] T. Graham, "On the absorption of dialytic separation of gases by colloid septa", Phil. Trans. R. Soc. Lond., 156, 399-439, 1866.