

Metallo-Dielectric Multilayer Sensor for Hydrogen Detection in Exhaled Breath

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Abstract: *A metallo-dielectric multilayer structure is proposed as a novel approach to the detection of hydrogen in the exhaled breath. Due to the bacterial overgrowth in the intestine, a spontaneous emission of H_2 is increased in the human breath when lactose intolerance occurs. By monitoring the changes in the optical properties of a multilayer palladium-polymeric structure one is able to detect a patient’s disease and the level of lactose malabsorption.*

Introduction

The enhancement in expired hydrogen over the 20ppm baseline goes back to the fact that part of ingested carbohydrates and proteins is not absorbed or digested but is fermented to form hydrogen by bacteria settling either in the colon or, especially in the case of a bacterial overgrowth, also in the small intestine. Part of this hydrogen is dissolved in mucosal blood, transported to the lungs within few minutes and finally appears in the breath [1]. The most common test used to diagnose lactose malabsorption or other intestinal diseases is the hydrogen breath test. During this test, the patient ingests a large dose of lactose or other mixture, after which hydrogen levels in the breath are measured at regular intervals. A rise in hydrogen breath levels (>20 ppm over baseline) theoretically indicates increased gas production due to such a intestinal disease. Hence, by plotting the H_2 -concentration in breath over time after the ingestion of the solution, one is able to reveal a malabsorption or an intolerance condition. In order to realize a high sensitive sensor for H_2 breath test clinical diagnosis, we underline the importance of the selectivity in hydrogen sensing. This issue arises from the fact that, in the majority of field applications, as well as in the breath exhaled, the hydrogen has to be detected at the presence of other gases, i.e. oxygen and nitrogen in the air. Moreover the breath of healthy people contains nitrogen, oxygen, carbon dioxide, water

vapor and inert gases. The remainder of breath (<0.000001%) is a mixture of as many as 500 different compounds [2]. However pathologic conditions could alter the breath composition introducing other gases and substances that can modify the sensor response. As a consequence, the presence of some traps for organic species is essential to preserve the detection mechanism from external damaging agents. A large number of materials and devices operating on different principles has been exploited for hydrogen sensing [3], such as modified metal-oxide resistive gas sensor [4,5], pellistor [6] and ChemFET type [7] devices. Several solutions of hydrogen sensors based on palladium sensitive properties have been proposed. It has been demonstrated that thin palladium film can be deposited on an optical fiber to detect few hydrogen quantities [8,9]. The measure of hydrogen concentration by monitoring the reflectivity of a thin palladium film positioned on the tip of an optical fiber [10] or looking at the optical transmittance of a thin palladium film grown on a glass substrate [11] is also possible. Finally, more sensitive, but also more complex, is the monitoring of optical changes by surface plasmon resonance measurements [12] or interferometric ones [13].

In this paper we propose a novel approach to the inspection of hydrogen concentration that results in a new device useful for H_2 -breath-test analysis. In fact, a palladium-dielectric multilayer structure reacts with small quantities of hydrogen in the human breath changing reversibly its transmission spectrum. The changes in the transmittivity involve certain wavelengths inside the spectrum and depends on the capability of the palladium films to absorb hydrogen particles, i.e. the change of dielectric constant. Metallo-dielectric structures allow to increase the total amount of sensitive metal within the structure improving their transmission properties and reaching high sensitivity values compared to other Pd-film-

based configurations.

Palladium-Hydrogen System

A lot of transition metals such as nickel, palladium and platinum absorb hydrogen spontaneously, changing their optical properties as a function of hydrogen concentration. In the latter part of the 19th century it was demonstrated that Palladium shows larger absorption of hydrogen compared to iron or platinum or other transition metals and that it is possible to store a high quantity of hydrogen in the Pd lattice [14]. Free electrons states of Pd are filled by free electrons of the absorbed hydrogen, modifying the Fermi level and changing reversibly the electrical [15] and optical [16] properties of Palladium. This causes both the real and the imaginary parts of the complex permittivity of palladium decrease [17]. It was demonstrated that the complex permittivity of the palladium hydride film ϵ_{PdH} could be expressed as:

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

where ϵ_{Pd} is the complex permittivity of bare palladium and h is a nonlinear function that gets smaller as well as the hydrogen concentration is increased, having values between 0 and 1 [8]. It was also demonstrated that the Drude model could describe the hydride palladium optical properties as well [18]. The Palladium hydride is formed when palladium is exposed to hydrogen and an efficient dissociation rate occurs when hydrogen atoms are in contact with palladium surface. The palladium hydride film has different mechanical, electrical and optical properties than those of bare palladium. Moreover hydride palladium exhibits a different behavior depending on the value of the hydrogen concentration. The hydride palladium could be characterized by two different phases, the α phase and the β phase. The reversible α phase occurs at low hydrogen concentration and in the absence of hydrogen Pd is considered in the α phase as well. If the hydrogen concentration is increased, Pd is transformed in the β phase. The transition point does not depend only on the hydrogen concentration but also on the film thickness and temperature. The β phase is not reversible and introduces a hysteresis in the optical and mechanical parameters of the palladium film. The transition from α phase to β phase for a thin palladium film (10-100nm) crops up at wider hydrogen concentration values (more than 4%) [19]. For hydrogen sensing applications it is important to avoid the Palladium phase transition during the experiments. A H₂-breath-test is based on the detection of small quantities of hydrogen, ranging from 20 ppm for healthy conditions to 80 ppm or more for pathologic conditions. In the whole range of our investigation the palladium remains in the α phase, being reversible to repeat the measurements

with the same device without any phenomena of hysteresis or structural variations.

Metallo-Dielectric Structure Theory

In recent years it has been demonstrated that it is possible to realize one-dimensional photonic band gap (PBG) structures, containing a few hundreds of nanometers of metals, relatively transparent to visible light and opaque for infrared and ultraviolet one [20]. This interesting property could be useful for many applications, such as the development of optoelectromechanical systems [21], or the enhancement of the quadratic and cubic nonlinearities of metal [22]. Propagation of light through thick metal layers arises from the resonance tunneling phenomenon. This feature takes place for many metals belonging to the transition metals class (ranging from group III to group XII). Some of noble metals, such as Au, Ag or Cu, are relatively transparent within a transmission window located at the beginning of the interband transition from d band to conduction band [22]. The most important objective of a metallo-dielectric, multi-layer structure is to enhance the transmitted field respect to the transmission through an equivalent amount of metal in a certain range of wavelengths. In this way, one is able to use a large quantity of metal, up to ten times more than the skin depth, maintaining losses exceptionally small. In fact, the concept of skin depth as the distance at which the field intensity is decreased to $1/e$ of its input value, loses its sense in the case of a periodic structure, due to the presence of spatial discontinuities, that drastically modifies the physical properties of the structure [20]. The bandwidth and the spectral position of the zero reflection condition, i.e. transparent metal regime, can be tuned by properly choosing the thickness of each layer. One or two anti-reflection coatings can be efficiently dimensioned by calculating the phase shift induced by the metal within the structure to improve the transmittance [23]. High values of transmittance and an high sensitivity to the presence of small quantity of the analyte, i.e. hydrogen, are reachable by using Pd, which is a transition metal, inside a periodic, metallo-dielectric structure. Several configurations for hydrogen sensing using Pd have been proposed embedding a thin film of metal between an isolating film and the tip of an optical fiber [23] or coating a piece of fiber with the sensitive material [24]. As suggested by the theory of metallo-dielectric multilayer structure, we can increase the overall thickness of Pd in the whole device, keeping the device transparent to the visible light.

Device Modeling

An efficient detection of hydrogen, operated by a multilayer structure, requires the use of an inert dielectric material that should be permeable to the hydro-

gen. Moreover, one of the most important issues leading to the transparent metal regime across the visible range is that the real part of the refractive indexes of the dielectric and palladium must be markedly different; While the majority of commercial polymers is characterized by a relatively low real part of the refractive index, reaching values lower than 1.8 [25], a high refractive index material has been recently proposed and realized. This material, known as EXP0454, is a titanium dioxide-rich polymer having refractive index values equal to 2 in the whole visible range. This material shows high transparency, resistance to chemical attack [26] being permeable to hydrogen. In fact, by properly alternating EXP0454 and Pd one is able to exploit the properties of a metallo-dielectric structure in order to realize a high sensitivity hydrogen sensor. Low values of hydrogen concentration, under the explosive limit of 4.65%, can be easily detected by the palladium/polymeric device if the optical properties of the hydride palladium are properly analyzed. If the surrounding mixture of gases is composed of oxygen (30%), nitrogen (70%) and hydrogen (few ppm) only, we can extract information about the optical properties of the Pd films, in order to relate a pathologic condition with an optical response for the sensitive metal. A malabsorption condition or intolerance results in an increase from a baseline value of 20ppm in the exhaled breath. This value remains constant during the test for healthy people, and change dramatically after few minutes for patients which suffers from lactose malabsorption or lactose intolerance. For medical purposes, we have to consider hydrogen values ranging from 20ppm to 100ppm, which are typical values for pathologic conditions of lactose malabsorption [27]. Several works report on changes of optical properties of thin film of hydride palladium absorbing different hydrogen concentration [16,17]. To take into account the dispersion properties of bare Pd we use the Drude model. One of the most important issues of the works mentioned above is that the Drude model still remains valid to describe the dielectric constant of palladium, even if the hydrogen concentration is increased [8]. In order to express the Drude parameters as a function of hydrogen concentration, the dielectric constant of bare Pd thin film has been measured using different substrates and comparing the results in terms of transmittance and reflectance [28]. Once the nonlinear function h (see eq.1) is evaluated, the Drude parameters and the dielectric constant are calculated for all hydrogen concentration under investigation. The use of the multilayer, metallo-dielectric structure allows to increase the total amount of the sensitive material, i.e. palladium, and, at the same time, improves the transmittivity. More-

over the sensitivity of the sensor is defined by the following expression:

$$S = \frac{\Delta T_{peak} [\%]}{H_2 [ppm] \Delta H_2 [ppm]}, \quad H_2 [ppm] = 20, \dots, 100 \text{ ppm} \quad (2)$$

We have performed an optimization analysis of the key parameters of the structure, in particular the thicknesses of metal and polymer, in order to find a balance between the width of the whole structure and the transmission features, including the transmission peak bandwidth. Looking for a purposeful configuration, able to ensure good sensitivity in the whole range of investigation, we have analyzed different thickness values for polymer and for the metal. Among these values we found that the best compromise in terms of sensitivity, device compactness and linearity of the calibration curve is reached for a dielectric thickness equal to 110nm and metal thickness equal to 10nm. Therefore, the optimized multilayer structure is composed of five layers of 10nm of Pd alternated by 110nm of the EXP0454 polymer. This structure is embedded within two antireflection coatings of 60nm of the same polymer. The transmission spectrum of the structure is reported in Fig.1. It has been calculated using the standard transfer matrix method. Normal incidence, absorption and dispersion phenomena are considered in all the simulations. The transmission spectrum of the multilayer system experiences small changes as the H_2 concentration varies in the environment. For example, by increasing the concentration of hydrogen, transmittivity levels within the visible range increase. This phenomenon is strictly linked to the red shift of the plasma frequency and to the enhancement of the damping factor of the hydride palladium. We have evaluated an increase of 7,4% in terms of peak value when a malabsorption condition (the overtaking of the 20ppm baseline) is detected. Moreover, a total increase of about 15,6% of the transmission spectrum is revealed when the total amount of hydrogen in the environment grows from 20ppm to 100ppm (Fig. 2).

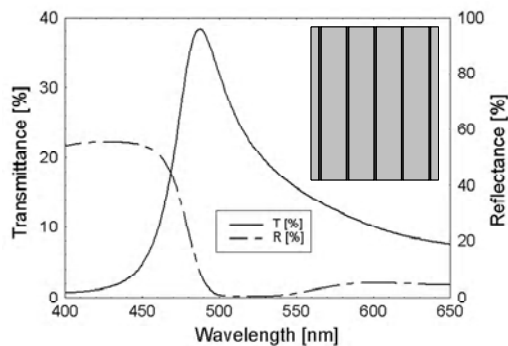


Fig.1: Sketch of transmission and reflection spectra for the multilayer structure. The inset shows the sensor structure: light grey regions are the dielectric layers (EXP0454) and dark grey regions are the metal layers (Pd).

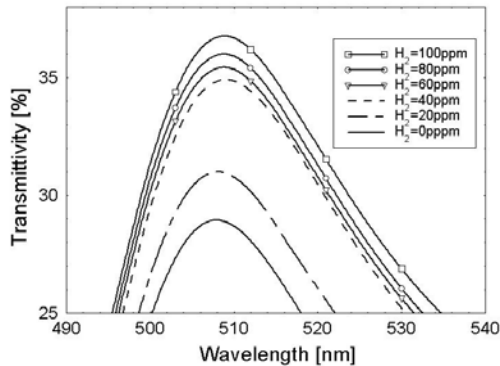


Fig.2: Transmission spectra for the optimized H₂ sensor: an increase of 7.4% in terms of transmittivity is noticed when a malabsorption condition occurs, i.e. the overtaking of the 20ppm baseline; the total increase of the transmittivity swelling the hydrogen concentration from 20ppm to 100ppm is about 15.6%.

Conclusions

We have proposed a novel approach to hydrogen sensing in order to realize a compact optical sensor suitable for the H₂-breath-test analysis. This kind of device is very useful for the detection of lactose malabsorption or intolerance condition, giving back a lucid information about the overtake of the healthy condition threshold. Moreover the proposed structure is appropriate to truthfully reveal the amount of hydrogen in the breath exhaled by unhealthy people, and can be proper to trace the relation between time and exhaled hydrogen.

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