Ultrasensitive and fast single wavelength plasmonic hydrogen sensing with anisotropic nanostructured Pd films

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ABSTRACT

Anisotropic nanostructured porous Pd films are fabricated using oblique angle deposition in vacuum on a glass substrate. They display a dichroic response, due to localised surface plasmon resonances (LSPR) within the nanoparticles forming the film, dependent on the incident light polarisation. Ultrasensitive hydrogen sensing is reached by using these films in conjunction with a differential optical technique derived from the reflectance anisotropy spectroscopy. The evolution of the samples' optical responses is monitored during the formation of Pd hydride in both the dilute α-phase and the dense β-phase, whilst the samples are exposed to different concentration of H_2 in Ar (from 100% H_2 to a few ppm). The measurements are performed at a single wavelength in the visible range and at 22 °C. The results show that a quantitative measurement of the hydrogen concentration in a carrier gas can be measured throughout the concentration range. The limit of detection is 10 ppm and the time for detecting the presence of H_2 in the carrying gas is below one second at concentration down to 0.25% of H_2 in Ar. Furthermore, the optical anisotropy of the samples and its evolution with exposure to H_2 are correctly reproduced with an effective medium theory.

1. Introduction

The development of hydrogen technology is today one of the main path to the production of clean and renewable energy [1–4]. However, the use of dihydrogen rises concerns from its explosive properties in air. 4% of H_2 is indeed the flammable mixture and thus efforts are made to develop selective, sensitive and fast responding dihydrogen detectors [5,6]. Several paths are being investigated to reach this goal [7–11] in particular with sensors based on Pd, as it selectively reduces when exposed to H_2 to form palladium hydrides [12]. In recent years, attempts have been made to develop plasmonic sensors, using localised surface plasmon resonances (LSPR) excited by light in metal-Pd or pure Pd nanoparticles (NPs), based on the change in optical response of Pd when forming hydrides [13]. In addition to the good sensitivity and fast response of such plasmonic sensors, the use of light as a probe implies that the sample is a passive component of the system, which eliminates hazards such as electrical sparks associated with electronic setups.

Most LSPR-based sensors [14–20] are made of Au NPs which exhibit a well-defined plasmonic resonance. Au NPs having weak interaction with H_2 [21], hybrid systems such as core-shell Au-Pd NPs [22,23], AuPd alloy NPs [20], Au NPs - Pd NPs oligomers [24,25] have been used. In these systems, the hydrogenation of Pd modifies the dielectric environment of the Au NPs, hence induces a shift in wavelength of the

LSPR of Au, which gives a measurement of the presence of H_2 [13]. Recently, K. Sugawa et al. have shown Pd to be the "third plasmonic sensing material". Indeed, LSPR in the visible range has been obtained by using large Pd spheres (diameters of 100–200 nm), displaying a dependency to the embedding medium's refractive index change, demonstrating the ability of Pd particles for plasmonic sensing [26]. It has also been shown that flat Pd nanodisks and nanorings of sizes around 300 nm, prepared by colloidal lithography, display LSPR in the near infra-red, which is red-shifted upon exposure to H_2, due to the formation of Pd hydride [27].

Despite this sensitivity to H_2, the thermodynamics of Pd hydride does impose an important limitation for hydrogen sensing applications. Indeed, the phase diagram of Pd hydride exhibits different phases depending on the partial pressure of H_2, $p(H_2)$. At room temperature, in the case of bulk Pd, the dense phase, PdH_x with $x \geq 0.6$, known as the β-phase, is obtained for $p(H_2)$ larger than about 10^{-2} bar, i.e. more than about 1% H_2 in ambient gas at atmospheric pressure. On the other hand, at $p(H_2) \lesssim 10^{-3}$ bar, only the low density α-phase is reached, with a maximum value $x \approx 0.02$ [28]. At intermediate pressure, a hybrid α + β phase is formed, constituted by β-phase regions embedded in the α-phase [29]. Regarding sensing applications, concentrations much lower than the flammability limit of 4% have to be detected, and it is therefore mandatory that H_2 sensors be sensitive to the very initial α-

phase formation [13]. This leads to an important issue for plasmonic sensors, as only the optical response of the dense β-phase strongly differs from that of pure Pd [30], whereas the optical response of the α-phase is very close to Pd. Consequently, shifts in the LSPR position large enough to be easily observed with conventional plasmonic sensors are reached only when the β-phase or the α + β phase are obtained, i.e. for p(H$_2$) larger than about 10^{-3}–10^{-2} bar at room temperature.

In the range of interest p(H$_2$) $\leq 10^{-3}$ bar, the α-phase leads to sub-nanometre shifts of the LSPR, which are difficult to measure with conventional plasmonic sensors. Indeed, the shift is usually determined by performing spectroscopic measurements around the resonance, followed by a fitting of the obtained spectra. Clearly, such a method is limited by the resolution and the reproducibility of the spectrometers which are, for current monochromators, depending on the width of the monochromator's slits, between 0.1 nm and a few nm. Improved resolution as low as 0.01 nm, necessary for detecting the α-phase, could be reached by using high-resolution monochromators with micrometre slit, though these apparatus are bulky and expensive, thus not suitable for simple, low-cost and easy-to-use sensors.

In order to answer these issues and to increase the sensitivity of plasmonic sensors, several authors developed specific Au/Pd or Pd nanostructures. For example, studies conducted by Langhammer's group showed a good sensitivity and reproducibility at 2% and 4% of H$_2$ in Ar as carrying gas for Pd NPs and Au-Pd heterodimers placed in a flow reactor [31,24]. Yang et al. reported a detection limit down to 2% H$_2$ in N$_2$ by using Au-Pd dimers and trimers [25]. With a "Pd-based plasmonic perfect absorber", Tittl et al. were able to detect concentration down to 0.5% [32]. Jiang et al obtained a detection limit as low as 0.2% for H$_2$ in N$_2$ with bimetallic Au/Pd nanorods [23]. Langhammer et al. [33] and Wadell et al. [20], indeed presented results with detection limit down to 0.1% of H$_2$, but the experiments were performed in a vacuum chamber and not at atmospheric pressure. To our knowledge, no LSPR-based system showed detection limit for partial pressures of H$_2$ in a carrying gas far below 1%, i.e. in the range of early formation of the α-phase, at or below 0.1%. Such sensitivity is desirable, for safety consideration but also for analysis of impurities in several industrial processes [6], as it has been brought forward by Wadell et al. [13].

In the present investigation, we address the sensitivity issue due to the resolution limitation of the monochromator, by using the Transmittance Anisotropy Spectroscopy (TAS), derived from the Reflectance Anisotropy Spectroscopy, which has been shown to be a very efficient and sensitive optical technique for investigating pristine or adsorbate-covered crystalline surfaces [34–38] and for supported metal NPs [21,39–41]. This method being differential, any kind of instability is eliminated, should it be due to the fluctuation in the light source or to mechanical noise. There is also no interference with ambient light and it can be used in illuminated environment. This technique leads to very stable and very sensitive measurements, which are not reachable with conventional plasmonic methods. Additionally, this apparatus is operated at a single wavelength and does not require spectroscopic measurements, which therefore frees oneself from the use of a monochromator and strongly lightens the operating system. Such an approach has been previously followed with anisotropic Au NPs dimers for the detection of biomolecules [42]. Similarly, by use of polarisation-dependent Au-Pd heterodimers, Wadell et al. have increased their sensitivity to H$_2$ detection and suppress drift issues [24]. However, in these examples, the NPs were prepared by lithographic methods, and the large size of the NPs reduced the overall detection limit to H$_2$ exposure. It has been shown indeed that the smaller the nanoparticles, the greater the surface-to-volume ratio, and the higher the sensitivity and the shorter the response time [13,43,44].

Consequently, efforts are to be made to develop smaller but anisotropic NPs, in order to exhibit fast response to hydrogen and be investigated by the TAS technique. We address this second issue by elaborating pure Pd films, grown by oblique angle deposition, as already proposed for other metals [45,46]. This method provides anisotropic

nanostructured films formed by NPs a few nm large, where the LSPR excited by the impinging light strongly depends on the polarisation of light, leading to dichroic properties suitable for TAS. We demonstrate that this yields a sensitivity to amounts of H$_2$ diluted in Ar as small as a few ppm at room temperature, and also a fast response in the range of seconds. Moreover, it also grants us the ability to determine the precise amount of small fractions of H$_2$ diluted in Pd, showing the quantitative potentiality of this technique. Experiments were also undertaken in dry and humid air (50% humidity) to determine perspectives in terms of selectivity and reactivity of the system in realistic conditions.

2. Experimental details

The elaboration of the anisotropic Pd films is done using oblique angle deposition under a 3.10^{-6} mbar vacuum on glass substrates, prepared from microscope slides cleaned with ethanol. The evaporation is carried out from a crucible heated by direct current with the samples positioned at a grazing angle of about 10° to the crucible and the evaporation rate was 0.2 nm/s. The mass thickness is controlled using a calibrated quartz balance and corrected to account for the evaporation angle. The characterisations of the samples are carried out by scanning electron microscopy (SEM) and optical measurements. The SEM apparatus used is a Zeiss Supra 40. The settings are EHT = 5 kV at a working distance of 2.8 mm with an aperture of 7 μm. The SEM needs to be adjusted with a low potential, as the substrate being nonconductive, the samples are prone to charging. The optical absorbance was measured on a Agilent Cary 5000 UV–vis-NIR spectrometer. Both parallel and perpendicular polarisations in relation to the sample's direction of evaporation are recorded. The anisotropic measurements are performed on a homemade TAS system. The TAS technique used here is derived from the RAS apparatus with Aspnes configuration [47], and measures the transmission anisotropy of transparent samples. Further details of the experimental setup can be found in Ref. [21]. The samples are investigated in a gas flow reactor equipped with a silica window enabling the TAS measurements during gas cycles. After purging of the cell with pure Ar for 24 h in order to eliminate any possible contamination, the samples are exposed alternately to pure Ar and to various H$_2$/Ar mixtures at atmospheric pressure. For this purpose, different concentrations of H$_2$ in Ar are prepared in a dedicated bottle by the following procedure. The mixture bottle is vacuumed whilst heated to 3.10^{-3} mbar for 24 h. It is then filled with 2.5 bar of H$_2$ and completed to 4 bar with Ar. The bottle is then emptied to atmospheric pressure and refilled to 4 bar with Ar. By using this procedure several times, accurate proportions of H$_2$ in Ar down to a few ppm can be obtained. The experiments in the gas flow reactor are undertaken at atmospheric pressures and at 22 °C, and the gas flows are fixed to 1000 sccm. These large flows are used to rapidly switch from pure Ar to the chosen concentration, and vice-versa. For measurements performed with dry or with humid air as carrying gas, a similar procedure for preparing the mixture is used.

3. Results and discussion

3.1. Microscopic and optical characterisations

The SEM image of a typical Pd film, obtained by vacuum deposition of Pd with mass thickness approximately equal to 1.9 nm is shown in Fig. 1a. The nanostructured Pd film is porous, and made up of elongated islands, separated by trenches. These islands appear to be formed by agglomerated NPs of size around 10 nm, separated by narrow gaps, and they are in majority oriented close to the direction normal to the evaporation orientation, indicated by the arrow. The morphological anisotropy of the film is better seen in the 2D Fourier transform of the SEM image (Fig. 1b).

The optical properties of the film are shown in Fig. 2, where the absorbance, given by $-log(T)$, where T is the transmission of the sample, is drawn for light polarisation either parallel or perpendicular