INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–10

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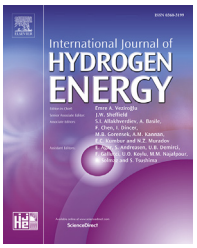

Room-temperature optical detection of hydrogen gas using palladium nano-islands

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ARTICLE INFO

Article history:
Received 17 November 2017
Received in revised form
26 January 2018
Accepted 29 January 2018
Available online xxx

Keywords:
Hydrogen detection
Palladium
Palladium oxide
Optical sensor

ABSTRACT

Palladium thin films of different thicknesses have been processed by oxidation and subsequent reduction in hydrogen atmosphere. Hydrogen optical sensing properties of as-deposited (Pd) and processed (r-Pd) samples have been experimentally tested with a H_2 concentration of 5% and 1%, discovering that the reduced films show improved performances in term of response/recovery time. As reveled by SEM images, the oxidation/reduction process modifies the surface appearance, which assumes a nano-islands structured morphology. The porosity of the processed films may explain the reduction of the response/recovery time, while the larger effective sensing surface in thinner samples justifies the responsivity performances.

Introduction

In recent decades, hydrogen has attracted great interest in the search for new and green energy sources [1,2]. Nowadays hydrogen is widely used in industrial processes, such as in food, chemical, semiconductor and transport industries [3]; the monitoring of its concentration is relevant for the control of key parameters in the industrial processes as well as for safety reason since hydrogen is an odorless, colorless, inflammable and explosive source when its concentration in air is above 4%. In particular, the immediate detection even of small concentrations is of fundamental importance in case of leaks from storage tanks and gas lines. Among the available sensing technologies [4], optical sensors are the most reliable and safe for applications in inflammable environments.

Palladium has been widely studied and employed as catalytic material in hydrogen sensors based on thin films [5–10], nanostructures [11–16] or plasmonic devices [17–19]. In such sensors, the high solubility of hydrogen into Pd induces the formation of hydrides which lead a marked and well-detectable change of the optical, electrical and structural properties of the hydrogenated metal [6,7,9]. In general, as the

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https://doi.org/10.1016/j.ijhydene.2018.01.183

sensing mechanism is directly connected to the dynamic formation of the Pd hydride, the sensing ability and the response/recovery time in Pd-based sensors depends on the properties of the hydrogen adsorption/desorption at the interface. In order to improve the native sensing performance of the Pd, different strategies were proposed. One of these methods is based on sensing films with modified morphology which can take advantages from an increase of the surface-to-volume ratio. For example, Pd-based mixtures comprising silicon dioxide (SiO_2), obtained by co-evaporating Pd metal and SiO_2 dielectric, have been also recently proposed for the fabrication of GaN-based hydrogen sensors. After removing SiO_2 by wet etching, a Pd film having a very high porosity was obtained, achieving enhanced performances in hydrogen sensing [20]. A second method, widely used to stabilize the mechanical issues due to the H_2 embrittlement and to improve the performance of resistive-type sensors, employs Pd-based metal alloys [21–25]. For example, recently a resistive-type senor based on a Pd-Ag alloy thin film showing a H_2 concentration limit of 100 ppm and a higher sensor response, reversibility, fast response time with respect to the sensors based on pure Pd films has been reported [26]. Valuable results were also obtained by mixing Pd with semiconductors or oxides [27–29]. For instance, Pd-SiO_2 thin films were suitable used in the realization of an high responsivity resistive-type senor characterized by a response-time in the 10 s–30 s range and a H_2 limit concentration up to 50 ppm [30].

In addition to the metallic Pd, different semiconductor oxides can be also employed as base material in gas sensing: PdO, SnO_2, ZnO, WO_3 are typical examples of semiconductor used for the detection of hydrogen [31–33]. Among these, palladium oxide (PdO) shows an interesting property as it undergoes a reduction process when it is exposed to hydrogen, returning metallic Pd. Recently, PdO and reduced palladium (r-Pd) films has been investigated for gas sensing [34]. The response to hydrogen was still monitored by measuring electrical resistance changes at room temperature. The r-Pd offered enhanced sensitivity thanks to the increase of the effective surface-to-volume ratio induced by the superficial nano-cracks formed during the reduction process. The PdO films were obtained by reactive sputtering deposition, while the subsequent reduction was simply obtained by exposing the films to hydrogen. PdO reduction during hydrogen exposure is irreversible at temperature below 100°, while at higher temperature a kinetic competition between PdO reduction and Pd re-oxidation occurs [35]. PdO nanoflakes based-sensors have been deeply investigated in this respect, showing that the real-time electrical resistance response has a dependence on temperature [35].

The present work investigates the potential use of PdO reduced films of different thickness for hydrogen detection at room temperature by using an optical reading approach instead of an electric/resistive one. Such all-optical sensors are particularly immune to electromagnetic interference and, in contrast to what is commonly done in electrical-based hydrogen sensors, they are intrinsically safe in explosive atmospheres because no heating elements are required. Pd samples were fabricated by e-beam evaporation, then oxidized by a thermal process carried out in vacuum and subsequently reduced in hydrogen atmosphere. The hydrogen response of the reduced samples was monitored by measuring the change of optical absorbance in the visible range (from 400 nm up to 800 nm). Results show a potential improvement in time-response of r-Pd with respect to standard Pd films.

Materials and methods

Pd films were deposited by e-beam evaporation of palladium pellets (99.95% purity) on 1 mm thick fused silica substrate. The deposition process was performed with a base pressure of 10^{-6} mbar (i.e. 10^{-4} Pa) while the temperature of the substrate was kept below 90 °C. The growth rate of the films was controlled by a quartz crystal microbalance and it was maintained at 0.5 nm/s. For each deposition run, three equal samples were fabricated.

Four different sets of samples, having thicknesses of 7.2 nm (S1), 12.6 nm (S2) and 17.5 nm (S3) and 27.3 (S4) have been prepared. For each thickness, some samples were oxidized by annealing at 500 °C in a vacuum at 1.5 mbar (i.e. 150 Pa); the oxidation process was performed in vacuum in order to improve the cleanness of the process and to guarantee a better control of the oxidation conditions. The annealing time was dependent on the film thickness (i.e. 1 h for each 10 nm) and it was determined to ensure the full oxidation of the films. Afterwards, the oxidized samples were exposed for 10 min to H_2 atmosphere (5% v/v nitrogen) at room temperature to obtain the r-Pd samples by inducing the reduction process described by the reaction:

$$PdO + H_2 \rightarrow Pd + H_2O \quad (1)$$

The thickness of the samples before and after the process was measured by a KLA Tencor P-16+ profilometer. The surface morphology and roughness were evaluated by a non-contact Park-System XE-70 Atomic Force Microscope (AFM).

The crystalline structure of the samples was investigated by x-ray diffraction (XRD) using a Philips PW-1729 diffractometer equipped with grazing-incidence x-ray optics. The analysis was performed at 3° of grazing incidence using Cu K-α Ni filtered radiation.

Scanning Electron microscopy was performed on a FEI Verios 460 L microscope operated at 1 kV and 25 pA. To avoid excessive charging of the samples, 1 kV of stage bias was applied.

The optical constants of Pd, PdO and r-Pd films were investigated by using a V-VASE Spectroscopic Ellipsometer (J.A. Woollam). Spectroscopic ellipsometry measures the complex reflectance ratio ρ, which is the ratio between the p-polarized and s-polarized complex Fresnel reflection coefficients. Such parameter is directly related to the optical constants n and k of the film, its thickness and surface roughness. The ellipsometry measurements have been fitted with a multilayer model, where the substrate optical behavior was taken into account as well as the superficial roughness as determined by AFM; the fused silica substrates were characterized prior to deposition. The films were modeled by using a dielectric function dispersion described by a combination of a Drude and a Lorentz oscillators in order to guarantee the

Please cite this article in press as: Corso AJ, et al., Room-temperature optical detection of hydrogen gas using palladium nano-islands, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.01.183