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In situ real-time investigation of hydrogen-induced structural and optical changes in palladium thin films

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ABSTRACT

In situ X-ray reflectance (XRR) and X-ray diffraction (XRD) were employed to finely characterise palladium thin films of different thicknesses during a hydrogenation process. The derived information was combined with *in-situ* ellipsometric measurements to achieve a complete knowledge of both structural and optical changes during hydrogen exposure. The films expansion, crystalline structure and optical properties modifications were characterised by de-coupling the mutual effects. The structural analyses revealed that when the palladium hydride formation is completed, the films undergo a relative thickness expansion of about 8–9%. This value is considerably larger than the relative lattice parameter increase reported in the literature; in the present work this discrepancy is partly attributed to the Poisson effect. Combining such results with the ellipsometric measurements, the palladium and palladium hydride optical constants were determined. Such results provide a general framework for monitoring structural and optical modifications of catalytic materials in reactive environments.

1. Introduction

Hydrogen (H_2) is involved in a wide range of applications such as in food, chemical, petrochemical industrial processes and medical diagnosis. For example, hydrogen storage is one of the most interesting technological innovations involved in the next-generation energy production [1,2]. The growing interest in hydrogen has driven the requirement for new technologies able to optimise its production processes, to reduce costs, and to improve the reliability and safety of hydrogen storage and distribution [3–5]. Unfortunately, H_2 is a highly flammable gas in air when its concentration is above 4%, and its use requires the development of detection devices able to monitor the environmental H_2 partial pressure. Among the available sensors, optical are the most reliable and safe for applications in inflammable environments [6]. The sensing material is a catalyst, which reacts by changing its optical and structural properties. Palladium (Pd) is one of the most interesting and widely used catalytic materials in hydrogen sensing devices [7–17]. In order to design and optimise such sensors and to interpret the experimental measurements, it's essential to know precisely the complex refractive index of the Pd hydride, which depends on the average hydrogen concentration through the Pd matrix. The change in Pd optical response is due to absorption of atomic hydrogen, after decomposition of its molecules at the metal surface, where the presence of atomic vacancies plays a fundamental role [18]. The hydrogen atoms, diffusing into the metal lattice, lead to the formation of Pd hydride [19]. At low hydrogen partial pressure, the number of atoms diffused into Pd is moderate and they are rather evenly distributed, giving the formation of a solid solution called α-phase; in this phase the distance between the hydrogen atoms is large and the compositional strain induced in the Pd lattice is weak [6]. When the hydrogen partial pressure increases, the number of hydrogen atoms in the metal, as well as their mutual interactions resulting from lattice strain and electronic

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interactions, also increase. At this stage, the formation of hydride (called β-phase) occurs in the metal regions where the concentration of hydrogen atoms becomes appreciable. As the hydrogen partial pressure increases further, the volume fraction of the β-phase increases as well, at the expense of the α-phase regions. For hydrogen concentrations above 4%, the hydride formation is considered complete [19]. During the formation of the hydride, both the optical and structural properties of the film experience a marked change. In particular, a considerable increase in film thickness occurs [20]. In most of the past works devoted to characterising the optical changes of Pd thin films upon hydrogenation, the optical constants prior to and after hydrogenation were derived by transmittance, reflectance and ellipsometric measurements, without taking into account lattice expansion [21–24], thus causing a systematic error in the determination of the optical constants of the Pd hydride. Recently, Yamada et al. pointed out the need to consider lattice expansion in the determination of PdH_X optical constants. However, they did not provide independent real-time measurements of the film thickness, which was instead taken as an additional fitting parameter in their ellipsometric spectroscopy model [25,26]. In the present study, *in situ* X-ray reflectance (XRR) and X-ray diffraction (XRD) were employed to finely characterise the Pd films. The derived information was combined with the *in situ* ellipsometric measurements. Such methodology represents a new approach in the investigation of Pd modification under H_2 exposure. Several papers have reported on structural modifications of Pd during gas exposure [27–29], but to the best of our knowledge, a real-time measurement of crystalline, optical and structural modifications during hydrogenation is presented here for the first time. The results obtained shed more light on hydrogenation phenomena. In particular, optical constants of PdH_X have been derived with a higher level of accuracy than in the previously published data. Finally, the films were characterised again after complete dehydrogenation in order to assess whether the initial optical and structural properties were restored. The results and methodology presented in this paper can provide a general framework for monitoring structural and optical modification of catalytic materials in reactive environments [30–36].

2. Materials and methods

Palladium films with different thicknesses were deposited by electron beam evaporation on 1 mm thick BK7 glass substrates. Before deposition, the substrates were cleaned by ultrasonic bath in acetone and isopropyl alcohol for 15 min and dried under nitrogen flow. The deposition process was performed with a base pressure of 10^{-6} mbar (i.e. 10^{-4} Pa) while the substrate temperature was kept below 40 °C. The films were obtained by evaporation of palladium pellets (99.95% purity). The film growth rate was controlled by a quartz crystal microbalance and was maintained at 0.6 Å/s. During each deposition run four identical samples were fabricated.

Films with different thicknesses were prepared, as shown in Table 1. Samples S1, S2 and S3 had thicknesses which are in the range for typical applications in hydrogen sensing; in particular S1 had the optimum thickness for inverted Surface Plasmon Resonance (iSPR) phenomena [37]. In contrast, S4 was a thick sample and could be considered a bulk structure. After deposition, the thicknesses of the films were determined using a profilometer, KLA Tencor P-16+, and the morphology of the surface was evaluated by a non-contact Park-System XE-70 atomic force microscope (AFM); all measurements are reported in Table 1.

One of the most interesting characteristics of the Pd films is represented by the possibility of re-using the samples through H_2 absorption and desorption. For this reason, all structural characterisations and optical constants were performed *in situ,* starting with measurements in air, then in a calibrated mixture of 5% H_2 and 95% Ar and finally repeated in N_2 atmosphere to assess the return of the film to its initial state.

Table 1
Summary of thickness, surface morphology and structure of the considered samples.

Sample	Thickness (profilometer)	Adhesion layer	Average surface roughness(AFM)
S1	12.4 ± 1 nm	None	0.9 nm
S2	20.9 ± 1 nm	None	0.8 nm
S3	40.4 ± 1 nm	None	1.0 nm
S4	112 ± 1 nm	Ti (2 nm)	1.4 nm

X-Ray diffraction (XRD) and X-ray reflectivity (XRR) using the Cu K-α (λ = 1.54056 Å) radiation were performed using a Philips MRD diffractometer, equipped with a parabolic multilayer mirror for primary beam conditioning and an Anton-Paar sample chamber which allowed investigation of the structural characteristics of the samples in a given atmosphere. The diffracted/reflected beam was measured as a function of the scattering angle by a proportional Xe counter, coupled to a Parallel Plate Collimator with an angular acceptance of 0.01°.

XRD measurements were carried out in grazing incidence mode, keeping the sample surface at an inclination of 0.5° with respect to the primary beam direction. The instrumental broadening contribution was measured using an Si polycrystalline standard. The collected data were analysed using MAUD software [38,39] in order to determine from the peak positions the lattice parameters of the deposited polycrystalline films. The Pd cell structure was assumed to be a cubic lattice (space group Fm-3m) with Pd atoms completely occupying a 4(a) site [40]. We also assumed arbitrary texture and a very simple isotropic microstructural model [41] in which only the average crystallite size and the root mean square (RMS) microstrain were considered adjustable parameters, in order to fit the heights and the widths of the diffraction peaks while keeping the number of free parameters as low as possible.

XRR measurements were taken for grazing angles ranging from 0.01° to 2.5°, with a step of 0.005°. The measurements were fitted using IMD software [42] assuming the film thickness, the material densities (both film and substrate), and the interface roughness. To carry out such fits, the Pd and PdH_X layers were modelled considering the atomic scattering factors provided by Henke et al. [43]; the interface roughness was described by the Nevot-Croce model [42].

Spectroscopic ellipsometry (SE) was performed by a VASE Spectroscopic Ellipsometer (J.A. Woollam). All samples were firstly characterised in air at three different incidence angles (55°, 65°, 75°) in the 400–1700 nm wavelength range, with a step size of 10 nm. Samples S1, S2 and S3 were also characterised in transmission mode in order to improve the precision of the extinction coefficient k determination. All the measurements in controlled atmospheres were performed at an incidence angle of 70°, as constrained by the flow cell geometry. The output of ellipsometric analysis is the ratio ρ of the total p-polarised to s-polarised complex Fresnel reflection coefficients of the sample, expressed in terms of the ellipsometric angles Ψ and Δ, according to:

$$\rho = \frac{r_p}{r_s} = \tan\Psi e^{-i\Delta} \quad (1)$$

which is directly connected to the material's optical constants and the structure of the sample [44]. When an isotropic and homogeneously absorbing film is thick enough, the refractive index components n and k can be derived directly by the experimental data