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Dielectric function of Pd hydride thin films in terms of hydrogen concentration and film's thickness: A parametric formulation

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ABSTRACT

An optimized parametric description of the dielectric function of thin granular Pd thin films is reported. The optical transmission spectra of 10, 15 and 20 nm thick films are measured and by means of an inversion procedure, the dielectric function of nano-sized Pd grains in the films is determined. Measurements are carried out for hydrogen pressures of up to 1 atm. The Brendel–Bormann model is used to describe in parametric form the dielectric function under these conditions.

1. Introduction

The development of hydrogen sensor prototypes, based on tuning the optical properties of nano-structured metal systems, requires both experimental arrangements and theoretical analysis [1]. Pd nanostructures are used as the sensing element in many of these systems [2], and the long-term stability of the systems is currently considered in order to develop devices that could be useful in a hydrogen based future economy [3]. Spectral measurements of light transmission through nanostructured hydrogen absorbing metal systems has proved to be a valuable tool to correlate the change in the intrinsic optical properties of the hydrogen absorbing materials with corresponding hydrogen pressures and concentrations [4]. The dielectric function (DF) changes when Pd absorbs hydrogen due to the variation of its band structure with insertion of hydrogen atoms at some of the interstitial sites throughout the metal lattice [5]. The knowledge of the Pd DF for a range of films' thickness involving nano-sized grains, and under increasing hydrogen pressures with corresponding concentrations of absorbed hydrogen, would be valuable for researchers working on design and optimization of nano-structured hydrogen sensors. The aim of this article is to provide such information. We obtain it from numerical inversion of transmission spectra when normally incident non-polarized light impinges on the surface of Pd nanostructured thin films deposited in a High Vacuum System (with a base pressure of 7.0×10^{-7} mbar) by electron beam evaporation on 1×1 cm^2 fused quartz substrates at room temperature (RT). The spectral trends observed in the transmission measurements have proved to be consistent for the different samples analyzed. The mass thicknesses of the films were measured by a Quartz Crystal Microbalance (QCM), which was also used to calculate the atom hydrogen concentration, x = [H]/[Pd]. The hydrogen pressure in the chamber was increased slowly up to about 1 atm. All measurements were made at RT. The flowchart in Fig. 1 summarizes the procedure followed to obtain the mean DF of Pd hydride grains in thin films exposed to increasing hydrogen pressures.

This procedure is explained in detail in Ref. [6] and the equations used are explicitly given there. First, from a transmission spectrum ($T(\lambda)$ with $\lambda \in [240, 1050]$ nm), and by assuming, as first approximation, that the optical thickness t_o is equal to the mass thickness t_m, the effective DF of the film ε_f is obtained by applying a Spectral Projected Gradient Method (SPGM) to carry out the numerical inversion [7]. Then, by using ε_f and the DF for bulk Pd reported in the literature [8], the packing density p is calculated (see Eq. (1) in [6]). The optical thickness is recalculated using the value of p and used to recalculate the effective DF of the film. These steps are repeated until convergence is obtained. Values of $p \cong 0.92$ have been obtained for the films considered here. This value is used to apply the Bruggeman model (BGM) [9] to obtain the mean DF ε_m of the grains in the thin film (see Eq. (2) in [6]). The coexistence of α- and β-hydride phases in the grains is again modeled by the effective medium BGM to obtain the average atomic hydrogen concentration x (see Eq. (6) in [6]). Finally the spectral dependence of ε_m is modeled by the Brendel–Bormann model [10] optimizing the Drude and Lorentz parameters (see Eq. (5) in [6]) by application of a SPGM. This procedure has been applied to films of different thicknesses, under increasing hydrogen pressure in

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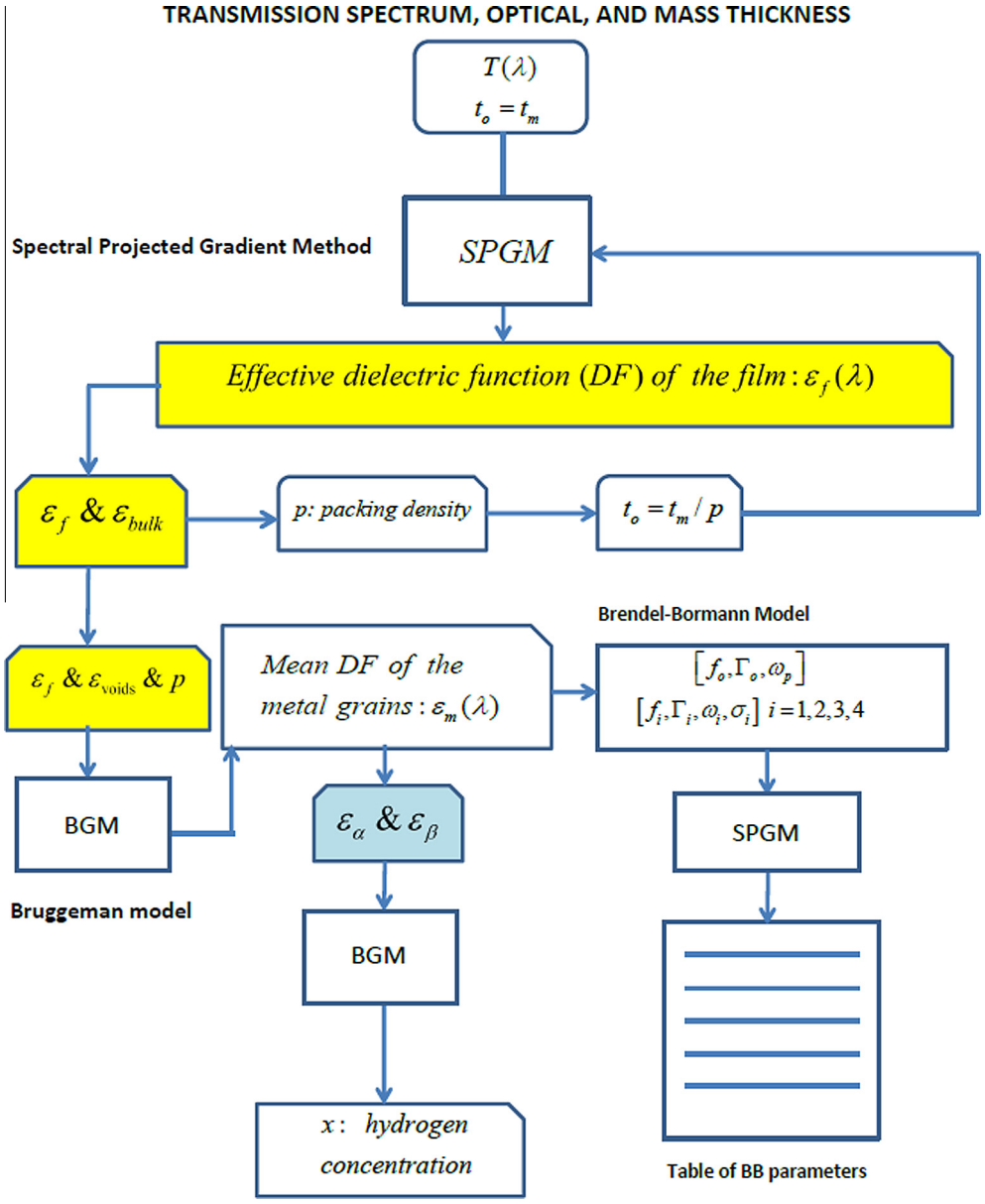

Fig. 1. Flowchart of the inversion procedure followed to obtain from transmission spectra the packing density, hydrogen concentration, and Brendel–Bormann parameters used to describe the DF of Pd hydride grains in thin films.

the chamber. In Section 3 we will report the first results of the analysis.

2. Correlation between hydrogen pressure and concentration

As mentioned, the mean DF of the Pd hydride grains in the thin film is determined by the presence of slightly hydrided regions (α-phase) and regions containing more significant amounts of absorbed hydrogen (β-phase). For a given angular frequency ω of the incident light, the effective medium BGM link the mean DF of the grains $\varepsilon_m(\omega)$ with those corresponding to the α and β phase regions, $\varepsilon_\alpha(\omega)$ and $\varepsilon_\beta(\omega)$ respectively [11]:

$$(1-f_\beta)\left(\frac{\varepsilon_\alpha-\varepsilon_m}{\varepsilon_\alpha+2\varepsilon_m}\right)+f_\beta\left(\frac{\varepsilon_\beta-\varepsilon_m}{\varepsilon_\beta+2\varepsilon_m}\right)=0, \quad (1)$$

where the volume fraction occupied by the hydride β-phase (f_β) is related to the hydrogen concentration through the relation $f_\beta = x/[x+(1-x)\gamma]$, with $\gamma = 0.886$ as the ratio between the volume of the conventional cell of the face-centered cubic (fcc) crystalline lattice of Pd and the volume of the fcc structure of PdH [12]. From the two previous equations one can obtain a weighted average hydrogen concentration given by:

$$x = \frac{\gamma\sum_{i=1}^{N}\dfrac{|\Gamma_\alpha(\omega_i)|\Delta(\hbar\omega_i)}{\sqrt{|\gamma\Gamma_\alpha(\omega_i)-\Gamma_\beta(\omega_i)|^2}}}{E_{\max}-E_{\min}}, \quad (2)$$

with $\Gamma_\alpha(\omega) = [\varepsilon_\alpha - \varepsilon_m]/[\varepsilon_\alpha + 2\varepsilon_m]$, $\Gamma_\beta(\omega) = [\varepsilon_\beta - \varepsilon_m]/[\varepsilon_\beta + 2\varepsilon_m]$, $E_{\min} = 1.18$ eV, and $E_{\max} = 5.17$ eV. N is the number of spectral measurements carried out ($N = 810$). Fig. 2(a) shows a set of measured transmission spectra for a Pd hydride film whose mass thickness is 10 nm, showing an increase of transmission with hydrogen absorption. Fig. 2(b) displays the relationship between hydrogen pressure and concentration. The dashed vertical lines indicate in an approximate way the limits of the α, $\alpha+\beta$, and β phases. Fig. 2(c) depicts the phase diagram when the hydrogen concentration is measured by the QCM method. In Fig. 2(b) the isotherm