

Interaction of the Electromagnetic Radiation with the Surface of Palladium Hydride Cathodes

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Abstract. The change of the electronic density of metallic Pd due to the hydride formation and to the build-up of the double layer, rising at the metal-dielectric interface when an electric field is applied, is involved in the variation of the metal dielectric function. A model including also metal surface roughness has been developed to take into account such modifications.

1. Introduction

The dissolution of hydrogen within a metal lattice and the formation of a metal hydride greatly perturb the electrons and phonons of the host material. Several are the relevant observed effects:

-The generally observed expansion of the lattice, often including a change in the crystal structure, involves a modification of the symmetry of the states and a reduction of the band width

-The attractive potential of the protons affects those metal wave-functions which have a finite density at the H site and leads to the so called metal hydrogen bonding band below the metal d-band

-The additional electron brought by the H atoms into the unit cell produces a shift of the Fermi level

-H-H interactions leads new features in the lower portion of the electron density of states.

One can affirm that the *1s* electron bonded with the hydrogen ion enters into *s* and *d* bands of the considered material, thus modifying the states density on Fermi surface and the energy bands structures itself^[1].

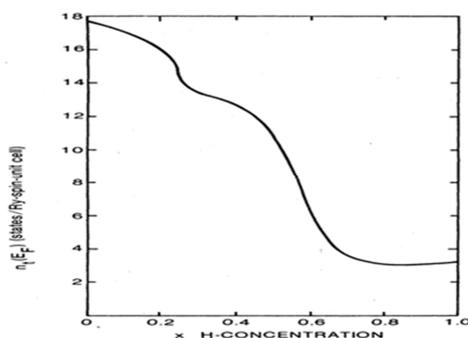


Fig. 1 - Total Density of States at the Fermi level plotted versus hydrogen concentration in Pd.

In Ref. [2] the total density of states (DOS) of palladium versus hydrogen concentration is shown, expressed for unit cell, spin and Rydberg (1 Rydberg, R_y , ~ 13.6 eV).

To estimate the electrons concentration n_e at Fermi energy for pure Pd and for $\text{PdH}_{x=1}$ we have to integrate the DOS with respect to such energy.

By considering that the volume of the unit cell in the reciprocal lattice is

$$V_{cell} = \frac{a^3}{4} \quad (1)$$

Where a is the lattice parameter, we can write for n_e the expression:

$$n_e \approx \frac{2DOS \cdot KT}{Ry} \frac{1}{V_{cell}} \quad (2)$$

Where K is the Boltzmann constant and T is the room temperature. By assuming a lattice parameter of 0.348 nm for pure Pd and of 0.406 nm for $\text{PdH}_{x=1}$ we obtain $n_{ePd} = 6.5 \cdot 10^{21} \text{ cm}^{-3}$ and $n_{ePdH_{x=1}} = 6.8 \cdot 10^{20} \text{ cm}^{-3}$. As expected, the electron concentration at Fermi energy strongly decreases in palladium hydride.

2. Electrochemical Surface Model

In the considered system, an electrochemical interphase has to be taken into account, as the hydrogen is introduced into metal lattice via electrolysis by a cathodic polarization of the metal.

The chemical interface is characterized by the presence of a strong electric field.

Recently, techniques based on the resonant excitation of surface plasmons (SPR) have been developed in order to study the effect of the electrochemical double layer electric charges redistribution on the thin metallic film dielectric properties^[3].

Substantially, the application of a electric potential modifies the dielectric properties near the metal-liquid interphase, and consequently the SPR signal is modified.

It has been demonstrated that the Helmholtz double layer formation deeply influences the SPR answer.

A model has been developed to take into account such modifications^[4].

Several effects, rising at a metal-dielectric interface when an electric field is applied, are involved in the angular shift of the SPR. In particular, the electronic density variations due to double layer and to the hydride formation are taken into account.

Modification in Palladium real and imaginary dielectric function components after deuterium solubilisation in metal lattice are shown in Fig.2 e Fig.3

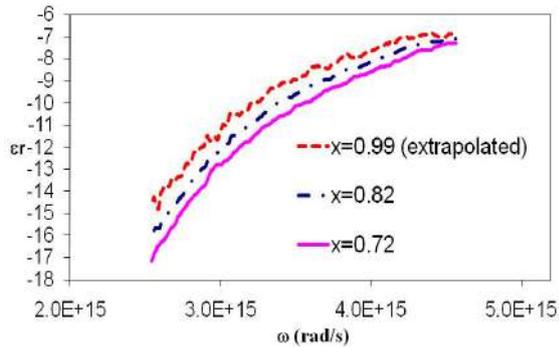


Fig.2 - Dielectric function real component, palladium

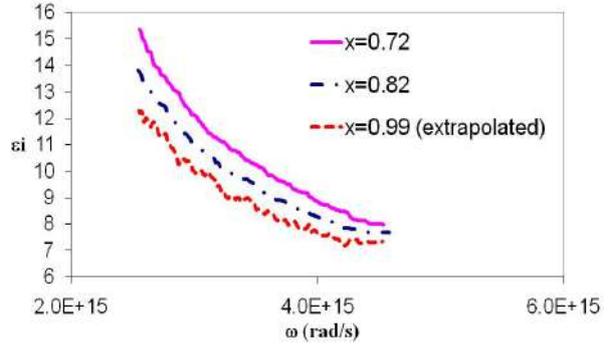


Fig.3 - Dielectric function imaginary component, palladium hydride.

Surface charge density σ , which can be calculated by the Stern's theory^[4], by varying the electronic configuration of the material, affected dielectric function value too^[5].

The dielectric function variation $\Delta\epsilon_{PdH_x}$ related to surface charge density is

$$\Delta\epsilon_{PdH_x} = \left(\epsilon_{x_{free}} - 1 \right) \frac{\Delta Ne \sigma_{PdH_x}}{Ne_{PdH_x}} \quad (3)$$

Where $\epsilon_{x_{free}}$ is palladium hydride dielectric function free electrons contribute, Ne_{PdH_x} is the free electrons concentration in palladium hydride bulk and $\Delta Ne \sigma_{PdH_x}$ is the free electrons excess on its surface, defined as:

$$\Delta Ne \sigma_{PdH_{0.99}} = \frac{\sigma^m}{q \cdot d} \quad (4)$$

Where q is the electron electric charge modulus and d the electric field penetration inside metal, defined in c.g.s. units as^[6]

$$d = \frac{c}{\sqrt{8\pi\mu_{0Pd}\rho_{PdH_{0.99}}^{-1}}} \quad (5)$$

Where c is light velocity in vacuum, $\rho_{PdH_{0.99}} \approx 5 \cdot 10^{-5} \Omega cm$ is palladium hydride samples resistivity and $\mu_{0Pd} = 1$ is palladium magnetic permeability.

The total surface palladium hydride dielectric function in electrochemical condition ϵ_{PdH_xTOT} can be expressed as:

$$\epsilon_{PdH_xTOT} = \epsilon_{PdH_x} + \Delta\epsilon_{PdH_x} \quad (6)$$

Where ϵ_{PdH_x} is palladium hydride dielectric function if no excess of charge is on the metal surface, i.e. no electrochemical processes are running.

In Fig.4 and Fig.5 the profile of PdH_x dielectric function real and imaginary components versus angular frequency is presented, in the range of validity of the proposed approximation. Also the total dielectric function, obtained taking into account the presence of an excess of electric charges due to electrochemical operating conditions is shown. As expected, the presence of surface charge density makes the material to acquire a more metallic behaviour.

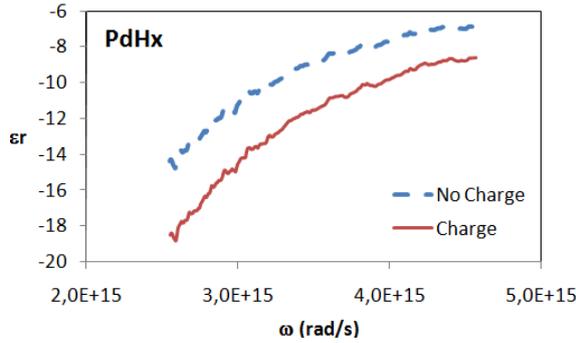


Fig.4 - Dielectric function real component, palladium hydride under cathodic polarization.

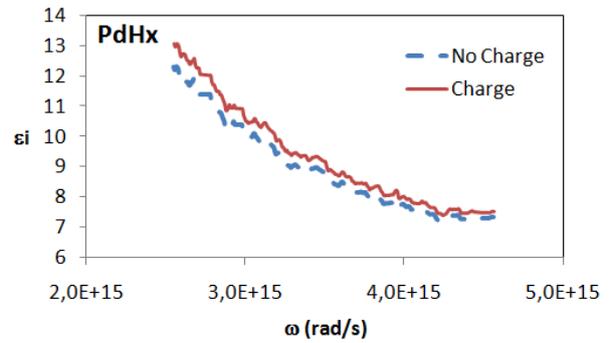


Fig.5 - Dielectric function imaginary component, palladium hydride under cathodic polarization.

Surface Plasmons resonance could give rise to a huge local field enhancement, due to a focusing effect: a broad e.m. wave is confined in a surface. Enhancement of about 10^2 factor could be obtained in this classical calculation. Using appropriate structures and quantum mechanical computation the enhancement factor could be equal to several magnitude orders. No matching condition results to be possible between light lines and surface plasmon dispersion curve at an air-Pd interface: the matching condition can not be satisfied on smooth surface, because the interaction between photons and plasmons can not simultaneously satisfy the energy and momentum conservation^[7]. It is possible to obtain s.p. excitation both using a corrugation lattice or by corrugating the metal surface itself: such a corrugation increases the surface parallel component of the laser beam wave vector, making thus possible the coincidence with s.p. wave vector^[7].

As Pd cathode are chemically etched before electrolysis, their surface is quite rough, with roughness parameters highly depending both from etching procedure and starting material properties. In Fig.6 and Fig.7 Atomic Force Microscope (AFM) three-dimensional images of two Pd etched samples are shown. The differences in surface morphology are quite evident.

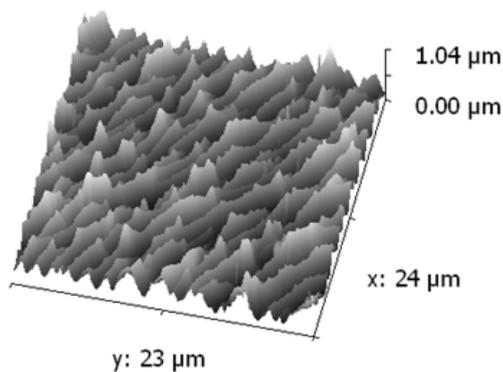


Fig.6 - Dielectric function real component, palladium hydride under cathodic polarization.

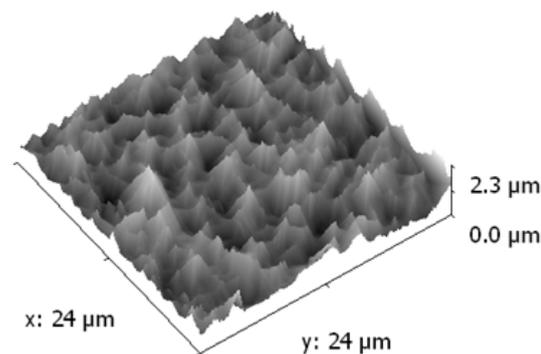


Fig.7 - Dielectric function real component, palladium hydride under cathodic polarization.

3. References

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