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# Dielectric function of palladium capped zirconium thin films as a function of absorbed hydrogen

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ABSTRACT

We report measurements of the optical transmission, between 240 and 1040 nm, and electrical resistivity of polycrystalline zirconium thin films as they absorb hydrogen. Both are measured as $H_2$ pressure is increased up to 880 mbar, at room temperature. Films, 20–22 nm thick, are deposited on fused quartz substrates by e-beam evaporation at $5.3 \times 10^{-7}$ mbar base pressure and covered with a 8.0 nm Pd over-coat. The morphology of the films is studied by means of AFM images. The complex refractive indices of Zr and Pd are extracted numerically from the transmission spectra by using a spectral projected gradient method for different hydrogen pressures. The corresponding dielectric functions for various Zr hydrogen concentrations are described with the parametric Drude-Lorentz and Brendel-Bormann (DL & BB) models. The Acceptance-Probability-Controlled Simulated Annealing approach is applied to calculate the parameters of the DL & BB model. This allows us to describe the effect of increasing hydrogen absorption on these parameters and in derived quantities, like the relaxation time and the effective mass of conduction electrons, the electrical resistance, the Fermi energy, and the electronic density of states at the Fermi level.



## Introduction

Hydrogen is absorbed by many metals and most of them have been extensively studied either for their fundamental interest or for their many technological applications. The formation of zirconium hydride has been reported since a long time ago [1] and subsequently this system has been extensively studied. Studies in the Zr–H system have identified three phases γ, δ and ε with nominal stoichiometric compositions of $ZrH_1$, $ZrH_{1.5}$ and $ZrH_2$, respectively [2]. Many works concerning the H-absorption effects on the Zr's structural, thermodynamic and elastic properties are reported, mostly motivated by the use of Zr and some of its alloys in the nuclear fuel industry. An extensive review of these studies is found in Ref. [3]. Information on the optical properties of Zr is available in the literature [4,5] but, to our knowledge, not on how these properties evolve as a function of concentration of the absorbed hydrogen. The objectives of this work are to provide experimental data on the dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, of Zr hydride for several hydrogen concentrations and to describe it in

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a framework that allows to reproduce $\varepsilon_1$ and $\varepsilon_2$ as a function of H-concentration and to interpret their changes comparing with, for example, band structure calculations. To these aims the real and imaginary parts of the dielectric function are extracted from optical transmission measurements and parameterized using a modified Drude-Lorentz model.

## Materials and methods

Zirconium (99.95% purity) thin films, about 20 nm thick, were prepared by e-gun bombardment at $P_{base} = 5.3 \times 10^{-7}$ mbar on fused quartz substrates (1 cm × 1 cm × 1 mm). A Pd cover layer, 8.0 nm thick, was deposited to protect them and catalyze hydrogen absorption. Hydrogenation is carried out *ex-situ* in a chamber equipped to simultaneously measure electrical resistance and normal optical transmission. The former was measured, both in the bilayer and the Pd overcoat, using the van der Pauw configuration [6]. The frequency of a calibrated quartz crystal microbalance, located in the chamber, on which a twin sample has been deposited, was recorded while $H_2$-pressure increased. The frequency change allows to estimate the hydrogen concentration: x = [H]/[Zr] [7]. For the highest $H_2$-pressure used, 880 mbar, we obtain x = 0.66, which means our measurements were made when a mixture of the α-Zr and γ-hydride coexisted, although the δ-phase may be also present in small amounts [2]. The completion of the γ-phase, i.e. x ≈ 1, is hindered by the thin film nature of our samples, since the clamping to the substrate reduces the maximum concentration obtained for a given pressure [8]. To obtain the transmission spectra as a function of hydrogen pressure, the bilayer was normally illuminated with non-polarized light in the wavelength range 240 to 1040 nm. The spectra were recorded with a fiber optic spectrometer (Avantes 2438) as $H_2$-pressure is increased. The resistivity and transmission results are shown in Fig. 1(a,b). All measurements were made at 22 ± 1 °C.

The base pressure just before hydrogenation of the Pd capped Zr films is close to $5.3 \times 10^{-6}$ mbar with the $H_2$ partial pressure smaller by at least one order of magnitude. Morphology images of an uncoated Zr sample were taken using an AFM (Vecco NanoScope 3D). They show a granular structure of the Zr film which consists of 345 nm × 254 nm x 18 nm average sized oval-shaped clusters. They appear to be made up of smaller grains of about one tenth the size of the clusters (see Fig. 2). This grainy structure of the films affects

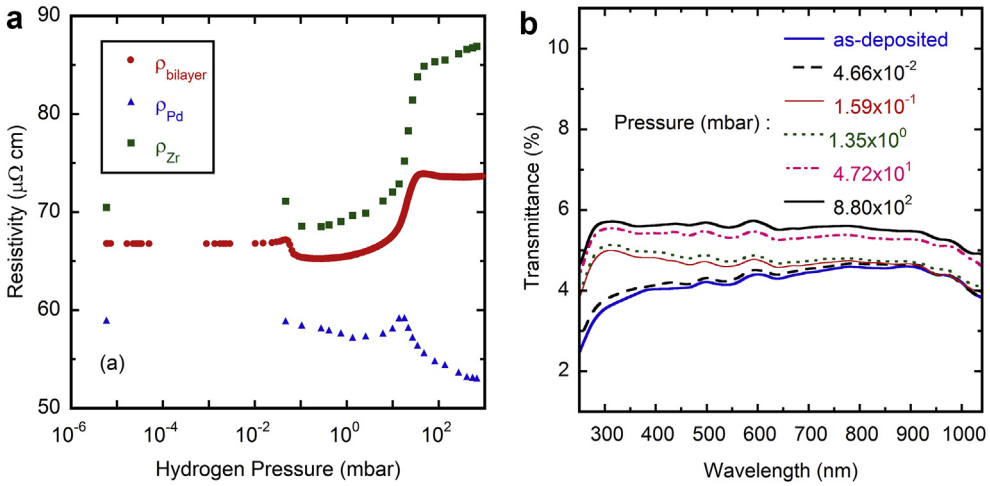


**Fig. 1 – Resistivity (a) and direct light transmission spectra (b) of a 20.3 nm thick Zr film covered with an 8.0 nm thick Pd overcoat are measured simultaneously as $H_2$ pressure is increased. The resistivity of Zr film (squares) is obtained by assuming a parallel arrangement between it and the Pd overcoat whose resistivity is measured (triangles) on a similar film. The optical spectra shown in (b) correspond to that taken from the as deposited film (lower solid line) and to those taken from the same film at sample $H_2$-pressures that illustrate the increase in transmission as hydrogen is absorbed.**

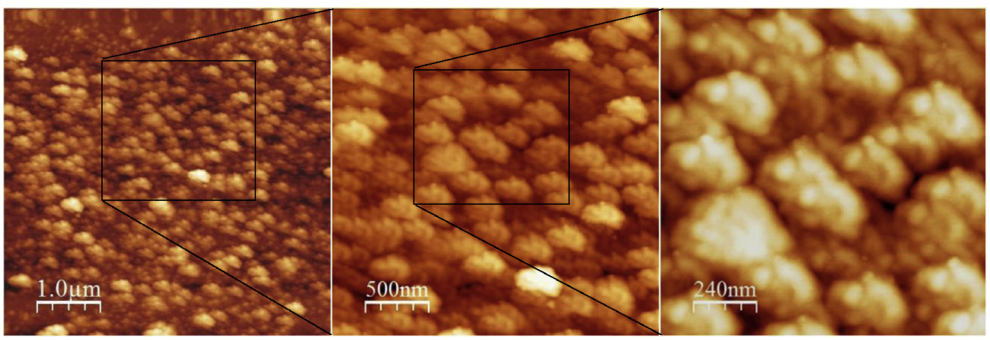


**Fig. 2 – AFM images of a 20.3 nm Zr film. The general granular structure of the film is clearly seen in the lower magnification image, and the shape and configuration of the grains become apparent at higher magnification.**

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