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Optical transmission and reflection of PdH_x thin films

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Abstract. Transmission and reflection data (0.5–5 eV) for 300 Å PdH_x thin films ($x = 0.65$, 0.85 and 0.92), hydrogenated under high-pressure conditions are presented and compared with similar data for pure palladium before and after hydrogen desorption. The main difference in transmission data consists of a pronounced peak around 1 eV in the transmission of PdH_x compared with the structureless continuously increasing transmission in pure palladium. This confirms the theoretical expectation of Khan and Riedinger that the inter-band absorption edge in PdH occurs at about 1 eV. The reflectivity data were measurable for PdH_{0.65} only; samples with higher hydrogen contents ($x = 0.85$ and $x = 0.92$) exhibit a reflectivity below 0.5%, which is thus not quantitatively measurable by the method applied. This high reduction in the reflectivity cannot be explained by the increase in surface roughness only. A possible contribution from hydrogen itself is briefly discussed.

1. Introduction

Palladium hydride (PdH_x) is the most thoroughly studied metal–hydrogen system. The imaginary part of the dielectric constant was evaluated theoretically for stoichiometric PdH (Khan and Riedinger 1982). The calculation was based on the band structure proposed by Papaconstantopoulos *et al* (1978a, b). As far as we know, only one experimental paper devoted to the optical properties of PdH_x has been published. Glosser and Frazier (1982) have measured the thermorelectance for PdH_x thin films with a hydrogen content x of up to 0.6. Structure at 4 eV was found in the β -phase region.

The reflectance measurements require bulk samples with a finely polished surface. It is more convenient to work with films, for which transmission and reflection data can be analysed simultaneously. Nevertheless, PdH_x lattice expansion during hydrogenation (3.5–5.5% in the β -phase (Baranowski *et al* 1971)) can lead to an increase in the film roughness and can reduce the reflectivity.

Direct comparison of the experimental data with the theory for PdH (Khan and Riedinger 1982) requires the preparation of films with a homogeneous hydrogen content close to stoichiometry. The most convenient and accurate method for achieving this requirement is the use of high-pressure gaseous hydrogen. Ion implantation can easily produce inhomogeneities in the hydrogen content as well as uncontrolled structure defects (Stritzker and Wuhl 1978). On the contrary, electrolytic charging can cause problems with surface contamination, especially when catalysts such as thiourea or arsenic oxides are used. In the latter case, codeposition of sulphur or arsenic with hydrogen is unavoidable.

The purpose of this paper is to present transmission and reflection data for PdH_x thin films with different well controlled hydrogen contents, including those close to stoichiometry (prepared under high-pressure conditions) and to compare them with the same data for pure palladium films before and after hydrogen desorption.

2. Experimental details

The palladium films 300 Å thick were deposited from a tungsten crucible by thermal evaporation of a 2 mm wire of palladium (0.999 purity) under high vacuum ($(1-5) \times 10^{-7}$ Torr) on optically polished Herasil silica glass plates. The thickness of the films was monitored with a quartz crystal microbalance with a 2.5% accuracy. The rate of deposition was 5–10 Å s⁻¹. The sample with the lowest hydrogen content ($x = 0.65$ (see figure 5)) was charged at a hydrogen pressure of 0.1 MPa. Higher hydrogen contents were achieved at high hydrogen pressures. The high-pressure device used consisted of a beryllium bronze cylindrical volume, supported by external steel rings (Baranowski and Bujnowski 1970). After introduction of the samples into the high-pressure volume at ambient air pressure, the working volume was evacuated to avoid contamination of the film surface (mainly by oxygen). Gaseous hydrogen was compressed up to 1 GPa in an external multiplier and then transmitted to the working volume by a beryllium bronze capillary. The pressure was measured with a calibrated manganin gauge. The construction details of this high-pressure device have been published elsewhere (Wyrzykowski and Baranowski 1988). All the films were hydrogenated at a constant temperature of 303 K. After about 1 h the whole device was cooled with liquid nitrogen. First, then, the pressure was reduced and the samples quickly taken out and kept continuously in liquid nitrogen. This procedure enabled us to avoid partial desorption of hydrogen during the pressure release. This is of special importance owing to small thickness of the films used and the corresponding small relaxation times for diffusion. These times can be estimated, from the value of Fick's diffusion coefficient at 300 K (10^{-6} cm² s⁻¹) and the activation energy of 27 kJ mol⁻¹ (Majorowski and Baranowski 1982), to be equal to 10⁻⁶ s at 300 K and 10⁸ s at 77 K.

To measure the hydrogen content in the PdH_x films up to a hydrogen pressure of 0.2 GPa, two 5 MHz quartz crystal microbalances were used, one of them coated with a palladium film. For 300 Å films deposited on both sides of the microbalance, this method gives a 3% accuracy in the hydrogen content. The details of this procedure have been published elsewhere (Wyrzykowski and Baranowski 1988). The film with highest hydrogen content was hydrogenated at a hydrogen pressure of 1 GPa, well above the pressure range where the microbalance was used. Graphical extrapolation of the data from lower pressures to 1 GPa gives a value of 0.91 for the hydrogen content, when assuming a linear dependence between the hydrogen content of the sample and the logarithm of the hydrogen pressure. This linear relation is known to be fulfilled at gaseous hydrogen pressures below 0.2 GPa (Perminow *et al* 1952, Wicke and Nernst 1964) but it fails to describe the hydrogen content in bulk palladium samples at higher hydrogen pressures (Baranowski 1978). Thus probably the above extrapolated value of 0.91 for the hydrogen-to-palladium ratio at a gaseous hydrogen pressure of 1 GPa is higher than the real concentration. On the contrary a molar ratio of 0.97 can be expected from the experimental results for bulk palladium samples (Tkacz and Baranowski 1976). During the cooling of the high-pressure device, before the reduction in hydrogen pressure, a further take-up of hydrogen is to be expected as a strong temperature dependence of

hydrogen absorption is well known for metallic palladium (Tkacz and Baranowski 1976). Nevertheless the lower solubility of hydrogen in thin films than in the bulk has been confirmed in many reports, where quartz crystal microbalance (QCM) as well as volumetric methods were used to detect hydrogen content (Frazier and Glosser 1980, Lee and Glosser 1985, Feenstra *et al* 1983). Moreover the superconducting transition temperature T_c was measured for the film hydrogenated at 1 GPa to obtain another independent determination of the hydrogen concentration in this film. We found $T_c = 3.7$ K which corresponds to the molar ratio of about 0.92 (Igalson 1978). Optical data were obtained on the double-beam computer-controlled spectrophotometer in the range 0.5–5 eV with 0.1% accuracy. The transmittance and reflectance were measured at normal incidence. A detailed description of the apparatus has been given previously (Rodzik and Kisiel 1983, Oleszkiewicz *et al* 1985). All the measurements of the PdH_x samples were performed at 77 K in a liquid-nitrogen optical cryostat.

3. Results and discussion

Almost all the published data on optical constants of pure palladium including bulk samples and films measured at room temperature or 4 K (Weaver and Benow 1975) agree on the observed structures. Nevertheless the calculated optical constants differ by a factor of 2 (Weaver 1975). The main reason for this is the difference in sample preparation. In order to compare our results with other results, the real and imaginary parts of the refractive index $n + ik$ were evaluated from the reflectance and transmittance of pure palladium films measured at room temperature on virgin (not hydrogen-treated) samples. A comparison with the results of Johnson and Christy (1974) for thin palladium films is presented in figure 1. Our results are similar to those of Johnson and Christy (1974), but the values of n at energies below 3 eV are lower in our case. However, for the films evaporated at rates lower than 50 \AA s^{-1} (for our films $5\text{--}10 \text{ \AA s}^{-1}$), Johnson and Christy (1974) observed lower values of reflectivity in the IR and consequently slightly different optical constants.

For reasons to be explained later the transmittance and reflectance data obtained for PdH_x films will be presented separately.

3.1. Transmittance of the PdH_x films

To clarify the difference between pure palladium and PdH_x, we start with the presentation of the transmittance of pure palladium film (before hydrogenation) (figure 2).

As can be seen, the transmission of pure palladium increases monotonically over the whole measured range. This transmission picture is a consequence of the monotonic decrease in absorption as shown in figure 1. The corresponding transmission curves for hydrogenated palladium are presented in figures 3–5.

There exist two main differences between figure 2 (pure palladium) on the one hand and figures 3 and 4 (PdH_x, where $x = 0.92$ and 0.85), on the other hand.

(i) The more or less continuous curve of transmission as a function of energy is contrasted with a distinguished peak of this quantity for PdH_x samples around 1 eV.

(ii) In contrast with pure palladium with a relative lower absorption in the approximate range 0.5–2 eV, PdH_x samples exhibit in the same energy range the highest transmission (both comparisons are with respect to the whole energy range discussed).

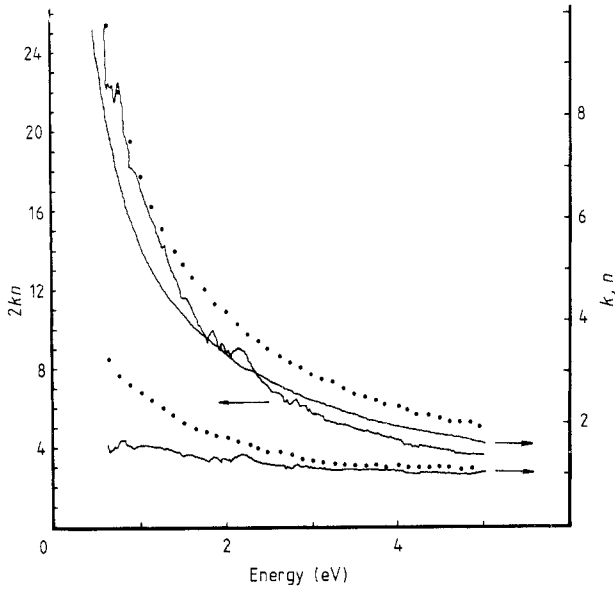


Figure 1. n and k values of the complex refractive index calculated from our reflection and transmission data for a pure palladium film (—, right-hand vertical axis) and from the paper of Johnson and Christy (1974) (●, right-hand vertical axis), together with $2kn$, the imaginary part of the dielectric constant, calculated from our n and k values (—, left-hand vertical axis).

Contrary to the very similar well distinguished transmission maxima around 1 eV for $\text{PdH}_{0.92}$ and $\text{PdH}_{0.85}$ (figures 3 and 4) the less hydrogenated sample $\text{PdH}_{0.65}$ exhibits a broad and less pronounced transmission maximum, as shown in figure 5.

Moreover the absolute values of transmission are much higher (from 4 to 16%) than those shown in figures 3 and 4 (3.5–8% and 2.5–5%). Thus in this respect figure 5 is related much more to figure 2 (pure palladium) than to the behaviours of the more

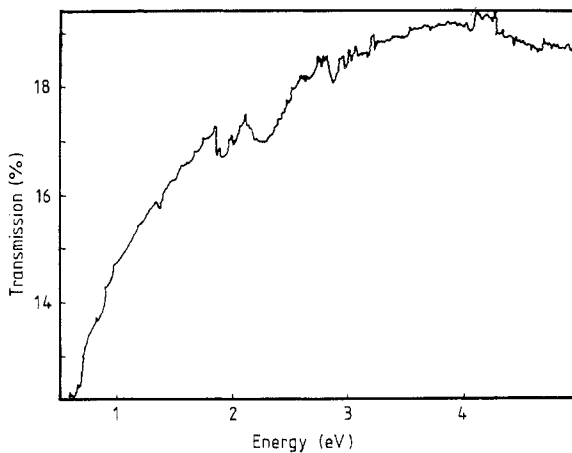


Figure 2. Transmission for a palladium film 300 Å thick at room temperature.

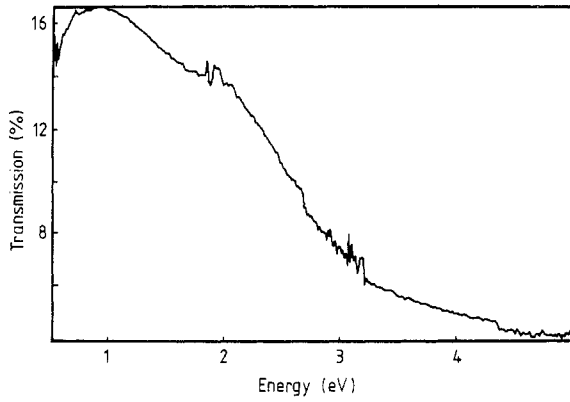


Figure 3. Transmission for a PdH_{0.92} film 300 Å thick at 77 K.

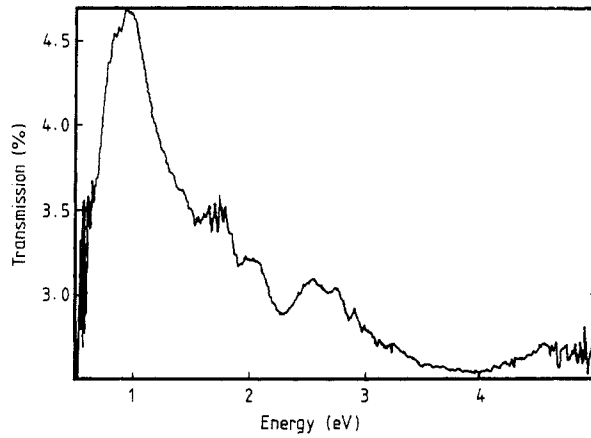


Figure 4. Transmission for a PdH_{0.85} film 300 Å thick at 77 K.

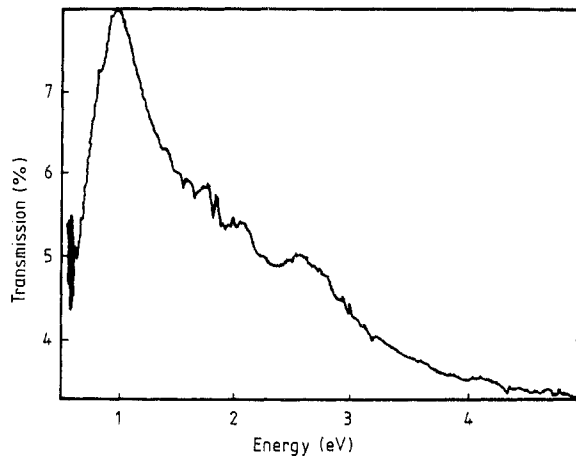


Figure 5. Transmission for a PdH_{0.65} film 300 Å thick at 77 K.

hydrated samples (figures 3 and 4). Because the hydrogen concentration in this film is close to that of the two-phase region, one cannot exclude the fact that phase segregation occurs, changing the overall transmission picture.

The differences in transmission data mentioned above in (i) and (ii) can be explained in the following way. A theoretical calculation of inter-band absorption in stoichiometric PdH (Khan and Riedinger 1982) places the absorption edge exactly at 1 eV. Moreover, because the free-electron absorption drops quickly in this region ($\sim 1/\omega^3$), a rapid decrease in absorption and consequently an increase in transmission is to be expected at around 1 eV. The fact that the transmission increase appears at around 1 eV for all three hydrogen concentrations discussed can lead to the conclusion that the position of the absorption edge is almost stable inside the β -phase region of the Pd-H system.

Although the theoretical calculations of the optical properties were performed only for stoichiometric PdH, some indications on the possible behaviour of the absorption edge can be found in band structures for substoichiometric PdH_x (Switendick 1972, Papaconstantopoulos *et al* 1978b, Faulkner 1976, Gellat *et al* 1978). The transitions with lowest energy are those from d bands to the Fermi level. The stability of the absorption edge position in the β -phase would mean relative stability of the positions of the d bands and the Fermi level. Indeed, many calculations for substoichiometric PdH_x support that picture (Switendick 1972, Papaconstantopoulos *et al* 1978b, Faulkner 1976, Gellat *et al* 1978). Anyway, only direct evaluation of the optical absorption for substoichiometric PdH_x will give a decisive response.

The strongest differences in absolute transmission values for all three hydrogen concentrations are in the IR region where free-electron absorption dominates. In the UV region, which is dominated by inter-band absorption, these differences are the smallest. Thus, one can conclude that free-electron absorption is strongly dependent on hydrogen concentration (contrary to inter-band absorption) and that this dependence is not monotonic (the lowest transmission values are for PdH_{0.85}).

The stoichiometric PdH, theory (Khan and Riedinger 1982) predicts three absorption peaks at 2.0, 3.4 and 5.5 eV. This can be partially attributed to the structures observed in the transmission data. For PdH_{0.92} as well as for PdH_{0.85} a small minimum at about 2.3 eV can be recognised. For PdH_{0.85}, there is a further flat minimum at around 4 eV. For PdH_{0.65}, all these structures are absent. Glosser and Frazier (1982) in their work on thermorefectance reported structure at 4 eV for PdH_{0.6} films measured at 45 °C. Although the structures observed at 2.3 and 4 eV are close to those predicted theoretically, they are rather weak. Moreover the structure at 2.3 eV exists also for pure palladium. Lafait *et al* (1978) claim that it is related rather to structure defects than to inter-band transitions.

3.2. Reflectance of the films

Figure 6 represents the comparison of the reflectivity of the palladium film in the UV region, before hydrogen absorption and after hydrogen desorption (hydrogen content $x = 0.92$). As can be seen, the reflectivity of the palladium film after hydrogen desorption is roughly three times lower (in the UV region) than the reflectivity of the same film before hydrogenation.

This reflectivity decrease can be related to the increase in the surface roughness during absorption and desorption of the hydrogen. Some workers (Bennet and Porteus 1961, Porteus 1963, Bennet 1963) have presented theoretical models where the formulae for the reflectivity changes due to different surface morphologies are evaluated. We can

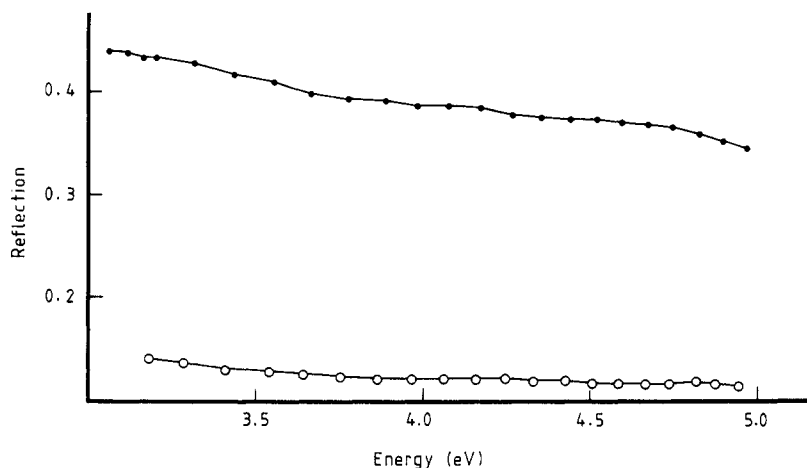


Figure 6. Reflection for a palladium film 300 Å thick in the UV region (●) and for a palladium film after complete desorption of hydrogen (hydrogen content $x = 0.92$) (○).

estimate the order of magnitude of the surface roughness σ (defined as the root-mean-square deviation of the surface from the mean surface level) using the simple equation (1) from the work of Bennet and Porteus (1961):

$$R/R_0 = \exp(-4\pi\sigma/\lambda)^2 \quad (1)$$

where R and R_0 are the reflectivities for the plane with roughnesses $\sigma \neq 0$ and $\sigma = 0$, respectively, and λ is the wavelength of the incident light. For the films after hydrogen desorption, R/R_0 is about 0.33 at 4 eV (figure 6). Then the calculated roughness (at 4 eV) equals 260 Å. This is a rather large value, comparable with the thickness itself. Hydrogen desorption, even when very slow, results in many cracks in the film structure. The reason for this is the hydrogen penetration at the film-substrate interface. The above facts can explain the large value of σ obtained. Although another more complicated formula (Bennet and Porteus 1961, Porteus 1963, Bennet 1963) can give a slightly different value, the order of magnitude will be the same. The UV energy range was used in the above calculation because the influence of the roughness on the reflectivity is strongest in this range.

One could expect the film thickness to be the maximum value for the film roughness. Then, if the decrease in reflectivity of the PdH_x film depends only on the surface morphology, the reflectivity changes should not be larger than that after hydrogen desorption. On the contrary, the reduction in reflectivity of the hydride phase was so strong that measurable values of the reflectance could be achieved only for the films with the lowest hydrogen content ($x = 0.65$) (figure 7).

This figure represents the reflectivity of the PdH_{0.65} film (full circles) compared with that of pure palladium (open circles). As can be seen, a continuous structureless decrease is found as a function of the energy. The values of the reflectance are too low to obtain solutions of the Fresnel equations for the real and imaginary parts of the refractive index (Nilsson 1968).

We can calculate the roughness for the PdH_{0.65} film using equation (1). The estimated value of R/R_0 is equal to about 0.14 in the UV region (if for R_0 we take the reflectivity of pure palladium; see figure 7). Then the calculated roughness (for 4 eV) equals 345 Å, i.e. larger than both the value for the film after hydrogen desorption (as calculated

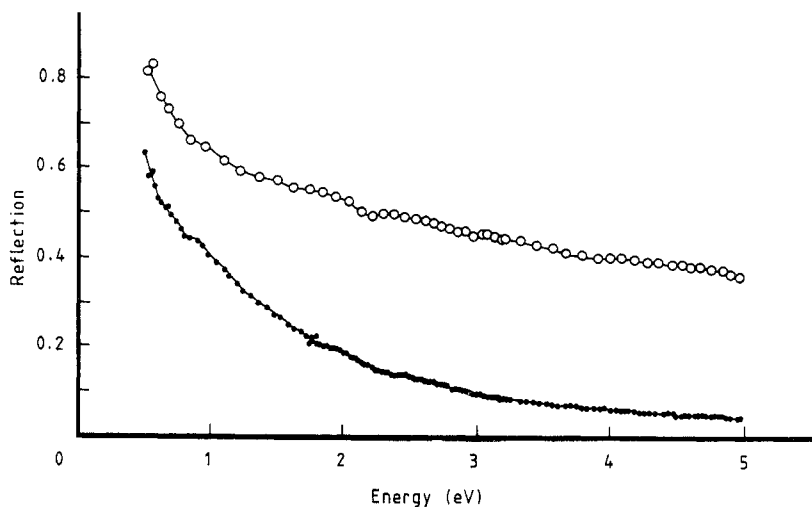


Figure 7. Reflection for a $\text{PdH}_{0.65}$ film 300 Å thick at 77 K (●) and for a pure palladium film 300 Å thick before hydrogen absorption (room temperature) (○).

above; see figure 6) and the applied film thickness. Obviously the corresponding values for the films with higher hydrogen contents ($x = 0.85$ and 0.92) would be larger because of the lower (below 0.5%) reflectivity of these films. Moreover the large decrease in the reflectivity of these films at higher hydrogen concentrations ($x = 0.85$ and 0.92) corresponds to a smaller further expansion of the PdH_x lattice (the transition from the α - to the β -phase, i.e. to about $\text{PdH}_{0.6}$, is accompanied by a 3% increase in the lattice parameter whereas further increases in the hydrogen content are characterised by smaller expansions).

This suggests that the surface morphology is not the only factor which contributes to the large reduction in reflectivity. Dignam and Moskovits (1972) analysed the influence of the adsorbed particles on the reflectivity of rough metal films. The decrease in adsorption-induced reflectivity appeared to be largely determined by the microscopic roughness characteristics of the surface. Although hydrogen adsorbed on PdH_x saturates well before formation of the β -phase (Wicke and Brodowsky 1978), its influence on the reflectivity depends on the surface morphology as well as on the optical constants of the PdH_x film. As these two factors change continuously with the hydrogen content, it is probable that the influence of the surface states on the reflectivity may be much stronger for some values of the hydrogen content.

4. Conclusions

We have presented transmission and reflection data for PdH_x films hydrogenated under high-pressure conditions. The main features of the transmission data reflect the theoretical expectations (Khan and Riedinger 1982). Nevertheless an anomalously low reflectivity of the films was observed, and the decrease in reflectivity was larger for the films with higher hydrogen contents. We suggest that adsorbed hydrogen can partially account for that phenomenon. Some results indicate that this is possible (Dignam and Moskovits

1972, Moskovits 1985). Unfortunately, all the experimental data presented so far for hydrogen adsorbed on PdH_x are for low hydrogen contents.

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