

Optical Response of Thin Supported Palladium Films to Hydrogen

NON-DESTRUCTIVE TESTING FOR HYDROGEN DETECTION

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Many variants of hydrogen gas sensors, based on the interaction between palladium metal and hydrogen gas, have been demonstrated in recent years, and the growing use of hydrogen as a raw material has promoted further activity in this area. This general interest led to our original motivation. Prior research, described in the literature, has been directed towards fabricating “sensors-on-a-chip”, by measuring changes in the electrical properties of thick palladium layers upon exposure to hydrogen: for example, values of their resistance or capacitance; the advantage here being that a signal is derived in an electrical form (1).

Signal recovery from sensors, based on direct electrical measurements, demands a continuous and hence a thick (> 100 nm) palladium film, which can be characterised in the range where bulk palladium properties dominate. These bulk properties are well understood (2).

However, our research took a different direction – by examining the response of extremely thin (~ 10 nm) palladium layers, in which deviations from bulk behaviour are known to occur, and we investigated properties of thin palladium film on silicon dioxide/silicon substrates, Pd-SiO₂/Si(3). As the electrical properties of very thin palladium films cannot be measured, due to the highly discontinuous nature of the films resulting from the low level of surface coverage, we turned to the use of simple laser diagnostic techniques (4). Our goal was to examine the performance of devices that might be compatible with the present day silicon-driven revolution in technology and with the use of lasers, thereby achieving a simple “sensor-on-a-chip” device, which would directly incorporate the sensor, source and detector in one component. In our experiments to date we have measured

changes in the absolute reflectivity of Pd-SiO₂ films upon exposure to various concentrations of hydrogen gas as a function of temperature, see Figure 1 (5).

Palladium-Silica/Silicon Structures

Silicon wafers (*p*-type 5–13 ohm cm) were cleaned, prior to palladium evaporation, by a standard technique. A layer of silicon dioxide was formed, by oxidation in dry oxygen at 1100°C, to a thickness of 100 nm. This process was followed by a 15 minute anneal in argon at the same temperature. Palladium was then evaporated onto the silica samples, which were kept at room temperature during the process. The Pd/SiO₂ film was not annealed before measurements were taken. The background pressure during the evaporation was $\sim 10^{-7}$ Torr, for a deposition rate of 2 to 3 Å per second.

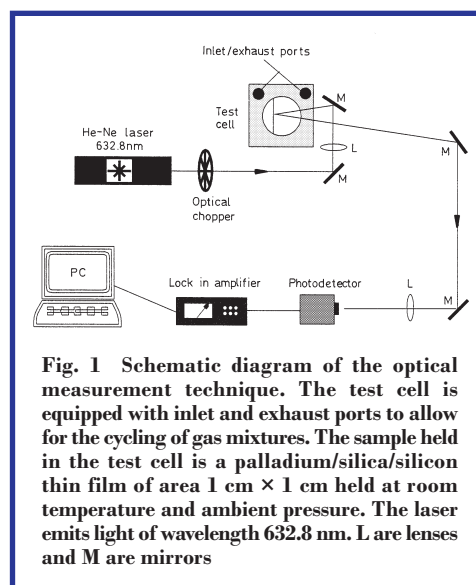


Fig. 1 Schematic diagram of the optical measurement technique. The test cell is equipped with inlet and exhaust ports to allow for the cycling of gas mixtures. The sample held in the test cell is a palladium/silica/silicon thin film of area 1 cm × 1 cm held at room temperature and ambient pressure. The laser emits light of wavelength 632.8 nm. L are lenses and M are mirrors

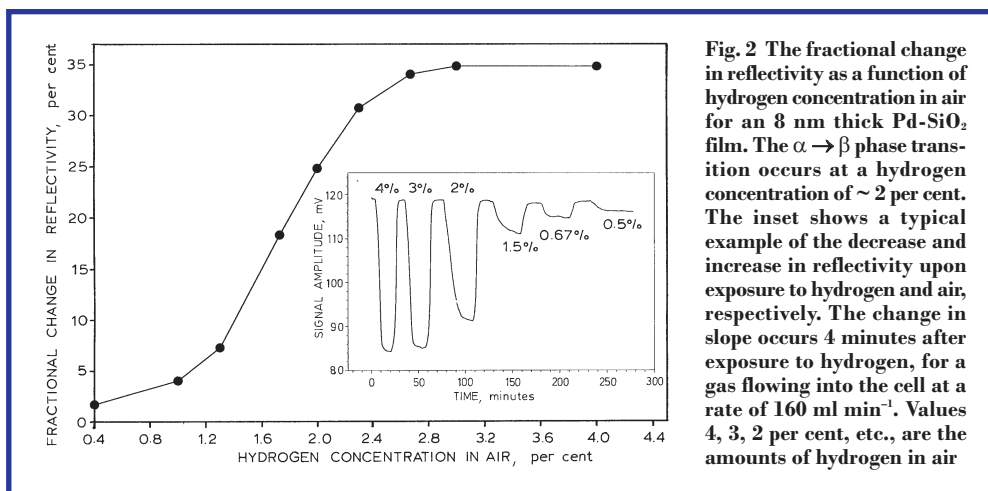


Fig. 2 The fractional change in reflectivity as a function of hydrogen concentration in air for an 8 nm thick Pd-SiO₂ film. The $\alpha \rightarrow \beta$ phase transition occurs at a hydrogen concentration of ~ 2 per cent. The inset shows a typical example of the decrease and increase in reflectivity upon exposure to hydrogen and air, respectively. The change in slope occurs 4 minutes after exposure to hydrogen, for a gas flowing into the cell at a rate of 160 ml min⁻¹. Values 4, 3, 2 per cent, etc., are the amounts of hydrogen in air

Measuring the optical properties of thin metal films is a complex issue, as they are very sensitive to the film deposition conditions and thickness, with the morphology and roughness of the film varying with thickness. Nevertheless, measuring the reflectivity of the film can prove to be a powerful and simple technique for deriving changes in the sample thickness. The absolute reflectivity, as a function of film thickness, is found to have a characteristic form (this is generic to all thin metal films regardless of the metal type) and can be classically modelled as a three-layer system (gas-metal-substrate) which behaves well, even for very thin nanometre-scale films.

The changes in the properties of the metal film depend on the exposure conditions to a particular gas, and can be derived from variations in the effective thickness of the film. Changes in the effective film thickness directly affect the phase of the light passing through the metal. The thickness variations also cause changes in the Fresnel reflection coefficients. However, in our case the film thickness is close to the penetration depth of the laser and changes to the phase of the light is the dominant factor.

The exposure of 8 nm thick Pd-SiO₂ films to hydrogen concentrations exceeding 2 per cent in air (at room temperature and pressure) produces a fractional decrease in reflectivity of up to 35 per cent. Purging the system with air

to remove the hydrogen gas results in the complete reversibility in the signal change.

The fractional change in reflectivity (FCR) is proportional to the hydrogen concentration both above and below 2 per cent, but with different slopes. Above a hydrogen concentration of 2 per cent, the FCR response is linear but almost flat, whereas, below 2 per cent the palladium exhibits a large increase in FCR response with increasing hydrogen concentration, and remains linear. The key result therefore is the observation of the room temperature changes in the composition of PdH_x which produce changes to the FCR.

The palladium-hydrogen system has two phases, the α - and β -phases, with a mixed phase region at room temperature, for which the α -phase extends to values where $x = 0.015$ and the β -phase to $x = 0.58$ (2). The β -phase marks a transition point at which the palladium crystal lattice undergoes a significant transformation with hydrogen concentration, see Figure 2. Therefore the $\alpha \rightarrow \beta$ phase transition occurs at ~ 2 per cent hydrogen concentration in air, causing the lattice to expand and thus allowing for further clustering of hydrogen at high densities. We have observed this phase transition for palladium film of thickness between 3 and 30 nm.

However, for films of thickness 1 to 2 nm, the graph of FCR with hydrogen partial pressure is linear and of constant slope at all measured

hydrogen concentrations, indicating that the sample is constrained to operate well within the α -phase, as there is plainly not enough material to allow for a comprehensive lattice expansion. This results from the island nature of the film.

We have also observed that for palladium films with thickness exceeding 30 nm, there appears to be a catastrophic failure in the response; this can be linked to the dimensional changes associated with the transition to the β -phase hydride.

The primary application of this technique – of using the fractional changes in reflectivity of palladium thin films to observe changes in the hydrogen content in the surrounding gas – will be for sensing various gases and monitoring the rate and degree of surface contamination of the thin sensing film. The laser technique can be applied to any gas-metal system.

We conclude by noting that this very simple

technique, namely monitoring the FCR of palladium films exposed to various hydrogen gas concentrations at room temperature and pressure, can recover important information regarding the properties of palladium thin films which would be impossible to make via electrical measurements.

References

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High Surface Area Porous Platinum Electrodes

Electrodes with high specific surface areas are needed in batteries, fuel cells and sensors for good efficiency and to aid in the production of small size devices. High surface area electrodes can be produced by controlled electrodeposition, by using the pores in lyotropic liquid crystals, by thermal decomposition of a precursor or by sputtering, the latter being suitable for complex objects.

Now, scientists in the U.S.A. have studied highly porous sputtered platinum dioxide, α -PtO₂, films as the precursor to high surface area platinum electrodes (L. Maya, G. M. Brown and T. Thundat, *J. Appl. Electrochem.*, 1999, **29**, (7), 883–888).

PtO₂ films 2–4 μm thick, were prepared by reactive sputtering using oxygen-argon, and then reduced to Pt either by room temperature exposure to a hydrogen-argon mixture or by electrochemical reduction. For comparison, Pt films were also produced by sputtering in pure argon.

The reduced films had density of 3.4 g cm⁻³, while the argon-sputtered films had density 16.3 g cm⁻³. The microstructure of the precursor films was porous and remained porous on reduction in hydrogen, which suggests a potential use as high specific area electrodes.

Electrochemical reduction of the oxide-derived film showed Pt, oxide and the gold substrate, which indicates it may be possible to use platinum dioxide as a medium for maskless generation of microscopic metallic Pt features using

scanning tunneling microscopy. The system could be used to fabricate Pt quantum dots of nanometre diameters for single electron devices.

MOCVD of Platinum Metals Films

The deposition of thin metallic and oxide films of platinum group metals via metal-organic chemical vapour deposition (MOCVD) is used for electronics, catalytic materials and advanced coatings. However, the films can be contaminated with impurities if precursors such as Pt(PF₃)₄ and (C₃H₇O₂PtMe₃)₂ are used and the MOCVD process has not removed them.

Now, scientists have synthesised a new precursor: methylcyclopentadienyl-(η^3 -allyl)platinum for platinum deposition (G. Rossetto, P. Zanella, G. Carta, R. Bertani, D. Favretto and G. M. Ingo, *Appl. Organomet. Chem.*, 1999, **13**, (7), 509–513). High quality and purity Pt films were deposited, probably due to the methyl-substituted cyclopentadienyl ligands being good leaving groups.

MOCVD has also been used to grow epitaxially conductive ruthenium dioxide thin films on LaAlO₃(100) and MgO(100) crystal substrates (P. Lu, S. He, F. X. Li and Q. X. Jia, *Thin Solid Films*, 1999, **340**, (1, 2), 140–144). Bis(cyclopentadienyl)Ru was the precursor and oxygen the reactant gas. The deposited films were crack-free, adhered well to the substrates and had room temperature resistivity of 40–50 $\mu\Omega$ cm.