Study of the thin-film palladium/hydrogen system by an optical transmittance method

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The thin-film palladium/hydrogen system was studied using a novel all optical method. Isotherms at room temperature (25 °C) were obtained for palladium films with different thicknesses. The measured isotherms included the α, α-to-β, and β phase regions. A decrease of the phase transition region was observed as the palladium film thickness was decreased. This optical method has good potential for use in studying the equilibrium and kinetic aspects of any thin-film/gas system. © *1996 American Institute of Physics.* [S0034-6748(96)03211-X]

I. INTRODUCTION

Understanding of isotherm relations is important for the further development of thin-film/hydrogen systems. These systems have potential applications in areas such as hydrogen storage,[1] Pd films as gate electrodes in metal–oxide–semiconductor (MOS) devices,[2] Pd films in photopyroelectric sensors,[3,4] and micromirror optical-fiber sensors.[5] Investigations of the behavior of thin-film hydrogen systems were carried out using the quartz crystal microbalance method[6,7] and the volumetric method.[8] The results showed that the isotherm relations differed from the ones for bulk palladium due to a larger contribution to the chemical potential from the surface free energy of a given phase when the film thickness is reduced.[6] These latter methods, however, usually require sophisticated equipment and instrumentation. Recently Wagner and Mandelis[4] suggested that the optical transmittance was the most sensitive optical mode when studying hydrogen absorption in thin palladium films. As a result of these observations, an apparatus was built to monitor the absorption of hydrogen in thin films by using the optical transmittance technique.

II. INSTRUMENTATION

The schematic of the experimental arrangement is shown in Fig. 1. The experiment consisted of four subsystems: gas supply, test cell, signal generation, and data acquisition. The gas supply component mixes hydrogen and nitrogen in a homogeneous flow. The flow rate of each gas can be adjusted and stabilized before the mixture is directed into the test cell. High purity hydrogen (99.999%) and zero grade nitrogen (99.9975%) from Matheson Gas Products were used. The test cell was made of aluminum and had a volume of 100 ml. This small volume helped to reduce the exchange time of the gas which is the time that takes the gas to reach the surface of the active element in the sensor. The test cell contained an

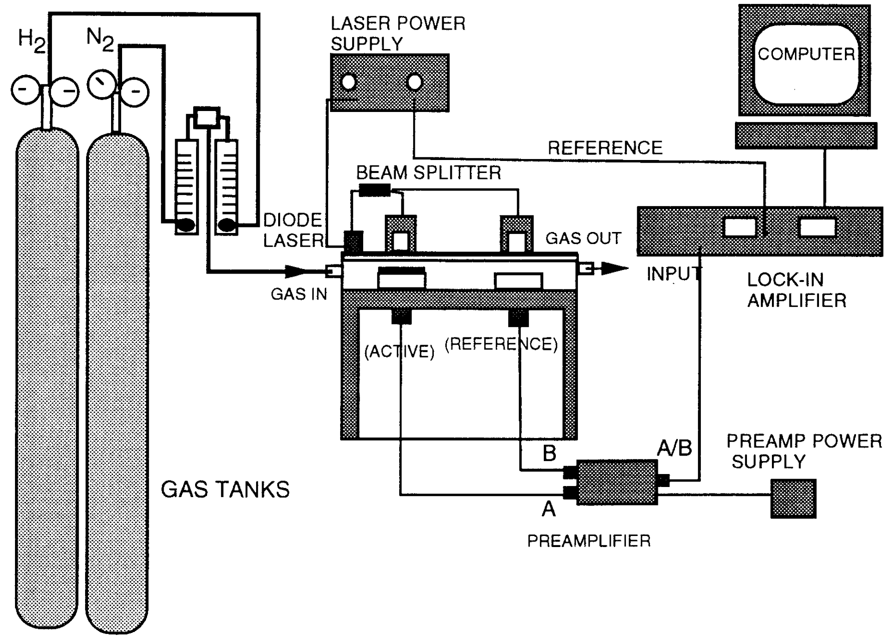

FIG. 1. Schematic of the experimental arrangement.

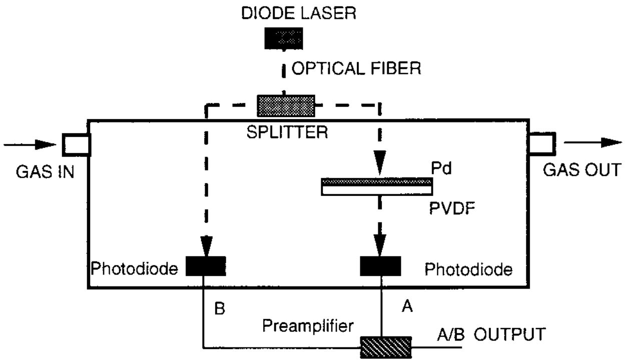

FIG. 2. Schematic of the optical transmittance method.

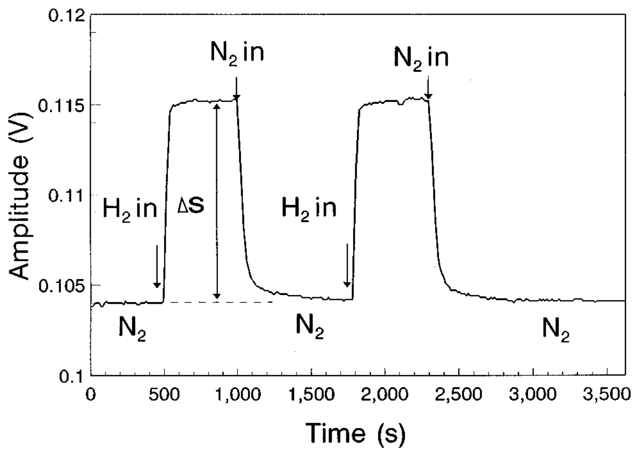

FIG. 3. Time-response profile from 10% (by volume) of hydrogen in nitrogen at 25 °C. The base line is 100% nitrogen. The saturation signal change ΔS used for isotherm construction is also shown.

active and a reference sensor. In this way any noise or drift due to the electronics was compensated by measuring the ratio of the active-to-reference signal. The active sensor had a 28-μm-thick polyvinylidene fluoride (PVDF) substrate coated on one side with a thin palladium film. The reference sensor had no substrate at all and was surrounded only by ambient gas.

A GaAlAs diode laser emitting at 850 nm, with a fiber-optic pigtail, was used to illuminate the palladium film. The diameter of the multimode optical fiber was 100 μm. In order to minimize fluctuations from the diode laser or its electronics, the optical fiber was connected to an integrated splitter that divided the laser beam into 90% and 10% components in separate fibers. The component with 90% of the beam was directed to the PVDF–palladium film and that with 10% was directed to the reference sensor. The two fibers were terminated with metal shell fiber-optic connectors. The optical fibers were mounted on the lid of the test chamber and lenses focused the beam onto the Pd–PVDF film. When the modulated laser light was incident on the palladium film, an optical transmittance (OT) signal was produced, as the film allowed some of the light to be transmitted to a photodiode. When hydrogen gas came into contact with the film, the hydrogen was absorbed into the palladium altering its optical properties.[4] The output signal of the photodiode from the reference and active sensors was connected to a current follower that converted the short circuit current of the photodiode into a proportional voltage. In the current follower the active signal was divided by the reference signal. Then the ratio of the two signals was input to a lock-in amplifier. The data acquisition was facilitated by a personal computer connected to the lock-in amplifier through an analog-to-digital (A/D) converter. A schematic of the sensor principle is shown in Fig. 2.

III. EXPERIMENTAL RESULTS AND ANALYSIS

Polyvinylidene fluoride films coated with various palladium thicknesses (50, 130, 260 Å), as specified by the manufacturer (AMP Flexible Film Sensors, Valley Forge, PA) were used. Concentrations of hydrogen in nitrogen ranging from 0.5% to 100% by volume were introduced into the test cell at room temperature (25 °C). A typical amplitude–time profile is shown in Fig. 3. The curve is for 10% hydrogen in nitrogen exposed to a 130-Å-thick palladium film. The isotherms obtained in this work for palladium films with various thicknesses are shown in Fig. 4. The vertical axis is on a logarithmic scale to emphasize the different phase regions shown in isotherms reported in the literature.[5,6] The solid and dashed lines shown in Fig. 4 correspond to the isotherms for the 60 and 180 Å palladium films reported by Frazier and Glosser.[6] At the time of this study no PVDF substrate with

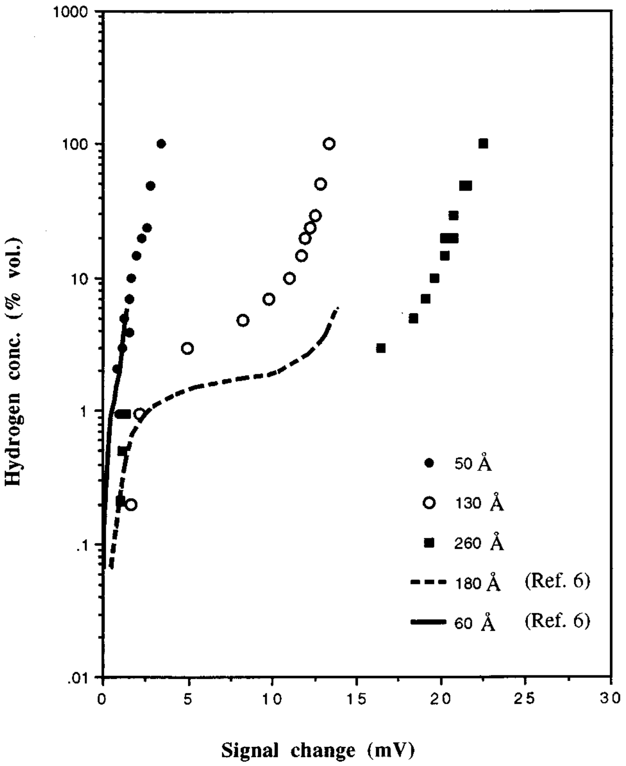

FIG. 4. Measured isotherms for palladium–hydride at 25 °C and various palladium film thicknesses. The solid and dashed lines correspond to isotherms for 60- and 180-Å-thick palladium films reported in the literature (Ref. 6).

palladium films of 60 and 180 Å thickness were available. Since no calibration of the sensor response in terms of the film composition (i.e., relationship between the saturation signal change, ΔS, and the H/Pd ratio) is at hand, the following relations were used: $\Delta S = 4.17 \times (\mathrm{H/Pd})$ and $29.4 \times (\mathrm{H/Pd})$ for the 60- and 180-Å-thick palladium films, respectively. These relations were obtained by making the maximum H/Pd ratios, reported by Frazier and Glosser,[6] correspond to the interpolated signal change, ΔS in mV, obtained from our measurements. The results suggest that the observed transmittance change is a measure of the composition of the palladium hydride, in agreement with reported reflectivity measurements.[5] The measured isotherms also indicated that the α-to-β region decreases in width as the palladium film thickness decreases, in agreement with reports in the literature that the chemical potentials of the α and β phases are in general dependent not only on pressure and temperature but also on crystallite size and the surface to volume ratio.[6–8]

IV. CONCLUSIONS

These results have important implications in the field of hydrogen sensors. The isotherm information may contribute to hydrogen safety through monitoring of the concentration range of interest (i.e., lower explosive limit) and optimization of the sensor response by modifying the design parameters, such as the palladium thickness. Also the method presented in this article represents a good alternative for studying the equilibrium and kinetic aspects of thin-film/gas systems that exhibit optical interactions with incident optical radiation. The method can, moreover, be used to study optoelectronic aspects of the Pd-hydrogen system, such as Fermi level shifts, localized deep hydrogen states, and interfacial phenomena.[9]

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[1] H. Wenzl, H.-H. Klah, and P. Meuffels, J. Less-Common Met. **89**, 489 (1983).

[2] H. M. Dannetun, L. G. Petersson, D. Soderberg, and I. Lundstrom, Appl. Surf. Sci. **17**, 259 (1984).

[3] A. Mandelis and C. Christofides, Sens. Actuators B **2**, 79 (1990).

[4] R. Wagner and A. Mandelis, Ferroelectrics **165**, 193 (1995).

[5] M. A. Buttler, Sens. Actuators B **22**, 155 (1994).

[6] G. A. Frazier and R. Glosser, J. Less-Common Met. **74**, 89 (1980).

[7] R. V. Bucur, V. Mecea, and T. B. Flanagan, Surf. Sci. **54**, 477 (1976).

[8] M.-W. Lee and R. Glosser, J. Appl. Phys. **57**, 12 (1985).

[9] G. Fortunato, A. Bearzotti, C. Caliendo, and A. D'Amico, Sens. Actuators **16**, 43 (1989).