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## An optical method to determine the thermodynamics of hydrogen absorption and desorption in metals

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Hydrogenography, an optical high-throughput combinatorial technique to find hydrogen storage materials, has so far been applied only to materials undergoing a metal-to-semiconductor transition during hydrogenation. We show here that this technique works equally well for metallic hydrides. Additionally, we find that the thermodynamic data obtained optically on thin Pd–H films agree very well with Pd–H bulk data. This confirms that hydrogenography is a valuable general method to determine the relevant parameters for hydrogen storage in metal hydrides. © 2007 American Institute of Physics. [DOI: 10.1063/1.2821376]

Energy storage, and particularly storage of hydrogen as an energy carrier, is a major issue for the possible implementation of a “hydrogen economy.”<sup>1</sup> Metal hydrides provide an attractive option to store hydrogen reversibly. The standard approach for the search of hydrogen storage materials is to synthesize bulk samples and to use volumetric, gravimetric or calorimetric techniques to follow the hydrogen evolution in the sample. The great disadvantage of this approach is that a bulk sample is needed for each investigated chemical composition. Thin films provide an interesting alternative to bulk, as heat and hydrogen diffusion issues are minimized by the thin film geometry. When thin film metal alloys are deposited in a combinatorial way, the surface science and optical techniques allow for a fast screening of the hydrogen absorbing compositions.<sup>2</sup> Recently we have determined the enthalpy and entropy of hydrogen absorption of thousands of different Mg–Ni–Ti compositions simultaneously by hydrogenography, our optical combinatorial technique.<sup>3</sup> While the as-deposited alloys are metallic, the different Mg, Mg–Ni, and Mg–Ti hydrides formed upon hydrogenation are all heavily doped semiconductors. This results in the opening of an optical bandgap. The large optical contrast in transmission in the visible range between the metals and the semiconductor hydrides facilitates the optical measurements. However, as some potential hydrogen storage materials may not undergo a metal-to-semiconductor transition, it is important to demonstrate the applicability of hydrogenography to metallic hydrides. For this we choose the archetypal Pd–H system that has been extensively studied in bulk,<sup>4–6</sup> cluster,<sup>7,8</sup> or thin film form.<sup>9,10</sup> The pressure-concentration isotherms (PCI) of Pd–H exhibit wide plateaus where the low hydrogen  $\alpha$ -PdH<sub>x</sub> phase coexists with the nonstoichiometric  $\beta$ -PdH<sub>x</sub> hydride phase. The 3.54% lattice mismatch<sup>11</sup> (11% in volume) between the  $\alpha$  and the  $\beta$  phases results in an expansion upon hydrogenation that generates large stresses and plastic deformation. This means that, upon cycling, the macroscopic Pd decrepitates into grains of a few micrometer size. While very thin films (thickness  $\leq 10$  nm) remain clamped to the substrate,<sup>12</sup> in thicker films most of the hydrogen compressive stress is released by the production of networks of large buckles (30–50 times the film thickness).<sup>13</sup>

In this letter, we present a method to record the hydrogen pressure-optical-transmission-isotherms (PTIs) of metallic hydrides. The method is demonstrated with the Pd–H system. The entropy  $\Delta S_0$  and enthalpy  $\Delta H$  of both hydrogen absorption and desorption processes are determined from the temperature dependence of the plateau pressure in the PTIs. The central result of this letter is that the  $\Delta S_0$  and  $\Delta H$  values determined optically are in remarkably good agreement with bulk values.

Polycrystalline Pd 65 nm thin films are prepared in a ultrahigh-vacuum dc magnetron cosputtering system (base pressure  $10^{-7}$  Pa, deposition pressure 0.3 Pa) at room temperature on  $70 \times 5$  mm<sup>2</sup> sapphire substrates. After deposition, metallic films are transferred into an optical cell to monitor their optical transmission during hydrogenation. The whole cell is placed in an oven to control temperature up to 300 °C. The gas pressure increase is controlled by a MKS 248/250 forward proportional-integral-differential system that regulates both inlet and outlet gas flows. The mixtures of 0.1% to 100% hydrogen in argon are used to achieve hydrogen (partial) pressures between  $10^{-1} < p < 10^6$  Pa. A 150 W diffuse white light source illuminates the sample from the substrate side, and a three-channel SONY XC-003 charge-coupled device camera continuously monitors the transmitted light as a function of hydrogen pressure. From Lambert-

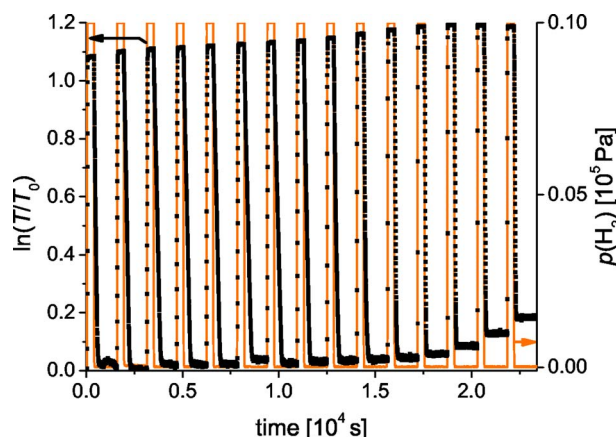


FIG. 1. (Color online) (squares), The optical transmission of a 65 nm Pd–H thin film over the first 15 hydrogen ab/desorption cycles. The hydrogen pressure (full line) is varied between  $10^4$  Pa (hold time: 600 s) and  $10$  Pa (hold time: 900 s).

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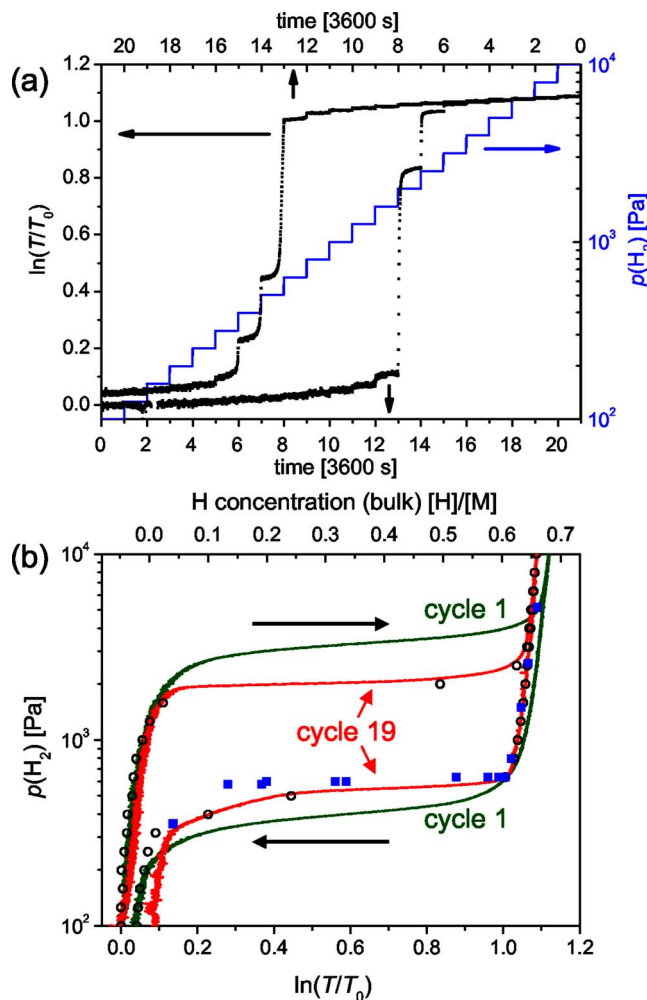


FIG. 2. (Color online) (a) (dots) Transmission of a 65 nm PdH<sub>x</sub> thin film as a function of hydrogen pressure steps at 294 K (cycle 18). Each pressure step (full line) is maintained 3600 s to ensure relaxation of the film with the hydrogen environment. The transmission  $T$  is normalized by the transmission in the as-deposited metallic state  $T_0$ . (b) (open circles) Equilibrium transmission after each pressure step in (a) (cycle 18). Full lines, ab- and desorption pressure-optical-transmission-isotherms for cycles 1 and 19 obtained by continuous sweeps of the hydrogen pressure at 294 K. (filled squares) Pressure-concentration-isotherm of bulk PdH<sub>x</sub> at 293 K.<sup>5</sup> The relation  $\ln(T/T_0)=1.47 \times c$  is used.

Beer law, the logarithm of the optical transmission  $\ln(T/T_0)$  is expected to vary linearly with the hydrogen concentration in a film of initial transmission  $T_0$ .<sup>14</sup> This is confirmed by joint electrochemical and optical measurements,<sup>15</sup> making possible the recording of PTI on hydrides presenting a metal-to-semiconductor transition.<sup>3</sup> These PTIs are analogue to PCIs obtained with standard volumetric or gravimetric methods.

The Pd bulk samples usually require an activation process before reproducibly absorbing/desorbing hydrogen. The standard procedure is to perform several absorption/desorption cycles before actually measuring a PCI. A similar procedure is applied here: for each cycle, the same hydrogen pressure ( $10^4$  Pa) above the  $\alpha \rightarrow \beta$  plateau pressure is applied and maintained until full absorption. Desorption is subsequently obtained by evacuating the cell. The optical transmission is recorded every 2 s to follow the kinetics of the process. Figure 1(a) shows the logarithm of the normalized transmission  $\ln(T/T_0)$  during the first 15 cycles at 295 K. The transmission at  $10^4$  Pa H<sub>2</sub> is approximately three times

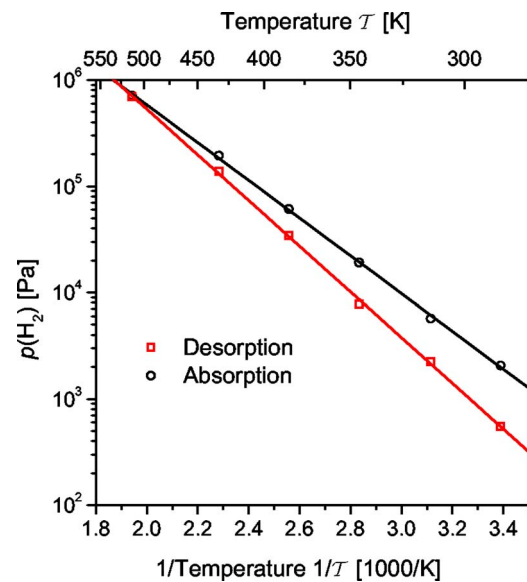


FIG. 3. (Color online) (symbols) Optically determined temperature dependence of the plateau pressure (Van't Hoff plot) in desorption ( $\beta \rightarrow \alpha$ ) and absorption ( $\alpha \rightarrow \beta$ ) for a 65 nm PdH<sub>x</sub> thin film deposited on a sapphire substrate. The full lines are the linear fit used to determine the enthalpies and entropies of hydride formation/decomposition.

higher than in the as-deposited state. This change corresponds to the transition from the  $\alpha$  to the  $\beta$  phase of PdH<sub>x</sub> and has been confirmed by x-ray diffraction. The transmission values in the absorbed and desorbed state are approximately constant up to cycle 8, after which both values increase with cycle number. Correspondingly, the absorption and desorption rates  $d \ln(T)/dt$  increase significantly for cycles 9–15. This intriguing behavior of both kinetics and transmission is directly correlated to the morphology evolution of the PdH<sub>x</sub> films. From scanning electron microscope (SEM) images (not shown) comparing the surface of the as-deposited state with the one after absorption/desorption cycles, we see that up to cycle 8 only large, unconnected buckles are present. After 15 cycles, a network of buckles and cracks enclosing areas of a few tens of micrometers has appeared. By continuously creating fresh, clean surface, cracks improve drastically the absorption and desorption kinetics for cycle 9 and following. As they extend throughout the film, they also contribute to the overall optical transmission.

After activation, PTI measurements are performed. To ensure (quasi-) equilibrium between the gas phase and H in Pd, the pressure is increased stepwise, letting the transmission relax during each step [Fig. 2(a)]. The transmission after each relaxation step is then plotted as a function of pressure to obtain an isotherm [cycle 18, empty circles in Fig. 2(b)]. Once the minimum relaxation time is known, subsequent PTI are recorded by continuous pressure sweeps of the same overall duration [cycle 1 and 19 in Fig. 2(b)]. The reproducibility of the isotherms of cycles 18 and 19 is good, demonstrating the equivalence of the stepwise and continuous procedures. Plateaus in pressure occur both in absorption and desorption, as a result of the coexistence of the  $\alpha$  and  $\beta$  PdH<sub>x</sub> phases. The PTI before (cycle 1) and after (cycle 19) activation at 296 K are also compared in Fig. 2(b). The hysteresis between absorption and desorption and the slope of the plateaus is significantly reduced by the activation. Recently, the reproducible hysteresis in metal hydride transformations has

TABLE I. Hydrogen desorption ( $\beta \rightarrow \alpha$ ) and absorption ( $\alpha \rightarrow \beta$ ) enthalpies and entropies for the Pd-H system.

$\Delta H_{\beta \rightarrow \alpha}$ [kJ(mol H <sub>2</sub> ) <sup>-1</sup> ]	$\Delta S_{\beta \rightarrow \alpha}$ [J(K mol H <sub>2</sub> ) <sup>-1</sup> ]	$\Delta H_{\alpha \rightarrow \beta}$ [kJ(mol H <sub>2</sub> ) <sup>-1</sup> ]	$\Delta S_{\alpha \rightarrow \beta}$ [J(K mol H <sub>2</sub> ) <sup>-1</sup> ]	Technique	Reference
-41.1±0.4	-96.0±1.2	-34.0±0.4	-82.4±1.0	Optical	This work
-41.2±0.8	-99.4±1.6	-36.4±0.8	-90.8±1.6	Gravimetric	Thin film <sup>a</sup>
-39.0±0.5	-92.5±1.3	-37.4±0.3	-92.5±0.8	Volumetric	Bulk <sup>b</sup>
-41.0±0.4	-97.5±0.8	...	...	Volumetric	Bulk <sup>c</sup>

<sup>a</sup>Reference 10.<sup>b</sup>Reference 4.<sup>c</sup>Reference 6.

been attributed to the coherency strain generated by the transforming phase.<sup>16</sup> In general, the total strain energy depends on the microstructure of the coexisting coherent phases. In particular, in buckled thin films there is much less in-plane additional strain energy involved during hydrogen absorption than in films fully clamped on the substrate.<sup>17</sup> The strain reduction induced by buckling and cracking is most probably responsible for the observed shrinkage of the hysteresis loop between cycles 1 and 18. In Fig. 2(b), the good agreement between desorption PTIs of cycles 18 and 19 and the bulk desorption PCI (Ref. 5) indicates that strain due to clamping to the substrate has been considerably reduced by the activation process.

In the subsequent cycles, PTIs are measured at various temperatures up to 500 K. The Van 't Hoff plots (Fig. 3) of the equilibrium plateau pressures are remarkably linear over 3 orders of magnitude in pressure. Enthalpy and entropy are then obtained from a linear fit of  $\ln(p_{\text{eq}}/p_0)$  versus  $1/T$ , according to the Van 't Hoff relation<sup>18</sup>

$$\ln\left(\frac{p_{\text{eq}}}{p_0}\right) = \frac{\Delta H}{RT} - \frac{\Delta S_0}{R}, \quad (1)$$

where  $\Delta H$  is the enthalpy of formation in kJ/mol (mol H<sub>2</sub>)<sup>-1</sup>,  $\Delta S_0$  is the entropy of formation in J K<sup>-1</sup>(mol H<sub>2</sub>)<sup>-1</sup> at standard pressure  $p_0 = 1.013 \times 10^5$  Pa,  $R$  the gas constant,  $T$  the absolute temperature, and  $p_{\text{eq}}$  the H<sub>2</sub> equilibrium plateau pressure of the PTI. The obtained desorption enthalpy and entropy values agree very well with the ones determined on bulk Pd (see Table I). While the absorption enthalpy value is close to experimental data as well, the absorption entropy is 8–10 J (K mol H<sub>2</sub>)<sup>-1</sup> less negative than other data reported in the literature. The critical temperature  $T_c = (\Delta H_{\alpha \rightarrow \beta} - \Delta H_{\beta \rightarrow \alpha}) / (\Delta S_{\alpha \rightarrow \beta} - \Delta S_{\beta \rightarrow \alpha}) = 528$  K is therefore lower than in bulk samples ( $T_c = 565$  K).<sup>5</sup> In thin films, residual clamping to the substrate is known to reduce the attractive long range H-H interaction and  $T_c$ .<sup>19,20</sup> However, the good agreement found between buckled thin film and bulk in desorption shows that thermodynamic quantities determined on thin films are relevant for the search for hydrides if the strain induced by clamping to the substrate is reduced by the proper activation procedure.

In summary, an optical method to determine the enthalpy, entropy and hysteresis of hydrogen absorption and desorption of thin metal films has been demonstrated for a metallic hydride. Pressure-optical-transmission-isotherms of the Pd-H system have been measured over wide pressure and temperature ranges. The method works for both interstitial hydrides, such as PdH<sub>x</sub> that remain metallic upon hydrogenation (this work) and hydrides that undergo a metal-insulator transition.<sup>3</sup> This shows that optical transmission can be used as a general screening tool for the combinatorial

search of hydrogen storage materials. This method is furthermore applicable to optimize hydrogen sensing materials,<sup>21</sup> catalytic caplayers promoting hydrogen uptake,<sup>22</sup> or smart coatings for adaptive solar collectors.<sup>23</sup>

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