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High-throughput characterization of hydrogen storage materials using thin films on micromachined Si substrates

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Abstract

A new characterization method is proposed for the development of hydrogen storage alloys, using thin films deposited on micromachined Si cantilevers with additional layers of SiO_2, Si_3N_4 and an adhesion layer. A sputter deposition system is used for deposition of thin films for hydrogen storage. The mechanical stress change due to hydrogenation, $\Delta\sigma_H$, leads to curvature changes of the film/cantilever combinations. These curvature changes are measured simultaneously on sets of cantilevers with an optical method in a gas phase hydrogenation apparatus, where the pressure can be varied from vacuum to a hydrogen pressure, p_{H_2}, ranging between 0.105 MPa and 5.1 MPa; the temperature can be varied from 20 °C to 450 °C. Thin films of Pd, Mg, Ti, Cr, and Fe were deposited for validation experiments. Isothermal measurements of thin film/substrate combinations are presented. The results show that the method is suitable for high-throughput characterization of combinatorial thin film libraries with respect to hydrogenation properties.

Keywords: Thin films; Hydrogen storage; High-throughput characterization

1. Introduction

For the future hydrogen economy, hydrogen storage is a crucial step from production to use, and it is considered to be one of the most technically challenging aspects. Compared to gaseous and liquid hydrogen storage, solid-state storage in materials such as metals or complex hydrides has several potential advantages, for example, in terms of volume or weight storage capacity, and safety [1,2]. But, none of the materials that have been found to date (e.g., [1,3]) are suitable for mobile applications, in which about 10 wt.% hydrogen should be stored at 0–100 °C and 0.1–1 MPa [4]. They either have low gravimetric density but can work near room temperature, or have high gravimetric density but sluggish kinetics and can only release hydrogen at high temperature [1,5].

One possibility for developing a new material with the desired properties is by controlling its chemical composition and microstructure on the nanoscale, for example, by controlled porosity [6], nanoscale grain sizes [7–9], or by multilayer [10,11] and nanolayer structures [12]. This can be done in an efficient way by depositing materials in the form of thin films, which avoids some drawbacks associated with bulk methods like high energy ball milling [13]. The number of possible materials for hydrogen storage is, however, very large. In order to identify the optimum material, many experiments have to be performed. In view of this background, it is evident that using combinatorial methods to study and develop new materials related to the hydrogen economy can be highly useful. Combinatorial methods [14,15] can be divided into deposition of materials libraries, and suitable high-throughput screening techniques, which rapidly measure the physical properties of interest of the materials in the library. Different combinatorial methods for the identification of hydrogen storage materials are currently being pursued [16–19]. In this paper, we propose to use an opto-mechanical method – based on the volume expansion of materials upon hydrogenation – as a screening tool for the identification of new hydrogen storage materials using thin films deposited in a combinatorial way on micromachined Si cantilever substrates.

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2. Opto-mechanical method for the characterization of hydrogen storage materials

The proposed opto-mechanical method relies on (a) the effect of volume expansion of materials upon hydrogenation, (b) fabrication and use of micromachined cantilever arrays and (c) a special set-up for simultaneous optical measurements of thin film/cantilever curvature changes due to hydrogenation.

2.1. Volume expansion and mechanical stress in thin films upon hydrogenation

The majority of materials which take up hydrogen have substantial volume expansion upon hydrogenation [20]. At a low ratio of hydrogen atoms to metal atoms, i.e. low hydrogen concentration c_H, hydrogen atoms occupy interstitial sites of the crystal lattice, which causes the expansion of the crystal lattice of the material. This volume expansion $\Delta V/V$ can be described as [20]:

$$\frac{\Delta V}{V} = c_H \left(\frac{\Delta v}{\Omega}\right) \tag{1}$$

and is proportional to c_H; Δv is the volume change per hydrogen atom and Ω is the atomic volume of a metal atom. The volume expansion upon hydrogenation can be as large as 20% per hydrogen atom to metal atom ($c_H = 1$) [20]. For cubic materials and small strains the change of the lattice constants, Δa, is by approximation:

$$\frac{\Delta a}{a} = \frac{1}{3}\left(\frac{\Delta v}{\Omega}\right) c_H = \alpha_H c_H \tag{2}$$

Thus, a linear relation should hold for the lattice strains with c_H upon hydrogenation with the proportionality factor α_H. At higher values of c_H, hydride phases can form and lead to coherency stresses. In thin films adhering to a substrate, the volume expansion leads to an in-plane mechanical stress and an out-of-plane strain. In the case of isotropic polycrystalline thin films with strong adhesion to the substrate, the in-plane stress (usually compressive) due to hydrogenation, σ_H, is related to c_H [21]:

$$\sigma_H = -\frac{E}{1-\upsilon}\alpha_H c_H \tag{3}$$

where $E/(1-\nu)$ is the biaxial modulus of the metal. The stress associated with hydrogenation of thin films can be remarkably high, on the order of several GPa (e.g., [22]). In the case of weakly adhering films these stresses can lead to delamination of the films from the substrate. High stresses σ_H can also shift chemical potentials for solution of hydrogen, and solubility limits [12]. Measured values of σ_H are usually lower than expected from theory, especially at higher c_H. This can be due to different stress relaxation processes such as formation of dislocations or stress-induced diffusion which can alter the film's microstructure [12,23]. Furthermore, it can be expected that the ratio $d\sigma_H/dc_H$ changes when hydride phases are formed at higher c_H [24].

In a thin film/substrate combination, where the film takes up hydrogen while the substrate is not able to take up hydrogen, a bending of the cantilever will be observed (Fig. 1). This is due to stresses in the thin film upon hydrogenation. This effect can be used for hydrogen gas sensing [25,26]. Here, we propose to use the bending effect as a screening tool for the search of new hydrogen storage alloys. In our experiments, thin film/cantilever combinations are arranged in an array (Fig. 2) and their curvature changes are measured simultaneously. Stoney's equation [27] is used to calculate the change of the mechanical stress, $\Delta\sigma$, from the curvature change of the cantilever:

$$\Delta\sigma = \frac{1}{6}\left(\frac{E_S}{1-\nu_S}\right)\frac{t_S^2}{t_f}\left(\frac{1}{R}-\frac{1}{R_0}\right) \tag{4}$$

where R_0 is the initial radius of curvature, R the radius of curvature during the experiment, t_S and t_f the substrate and film thickness, E_S and ν_S are the Young's modulus and the Poisson's ratio of the substrate, respectively. The total measured stress change, $\Delta\sigma$, is the sum of possible different stress contributions:

$$\Delta\sigma = \sigma_H + \sigma_{th} + \sigma_{str} \tag{5}$$

where σ_H is the stress due to hydrogenation, σ_{th} thermal stress and σ_{str} can be a stress contribution from structural changes.

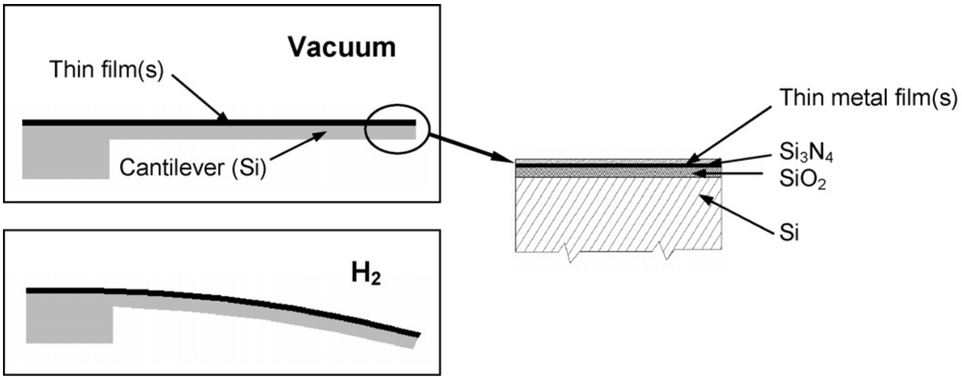

Fig. 1. Illustration of the measurement principle (not to scale): thin film/substrate combination showing a curvature change upon hydrogenation.

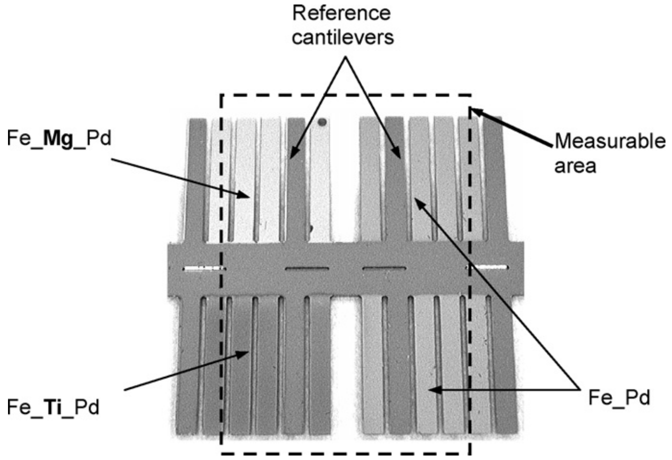

Fig. 2. Picture of a cantilever material library: 24 cantilevers are arranged in 4 quadrants, 16 cantilevers are simultaneously observable. Uncoated cantilevers serve as reference.

2.2. Fabrication of cantilever arrays

The new screening technology is based on micro-machined arrays of Si/SiO_2/Si_3N_4 cantilevers (Figs. 1 and 2), fabricated by photolithography, thin film deposition, and etching; 4-in. Si (100) wafers (thickness 400 μm) were used. Since Si forms silicides with many materials, additional layers (0.3 μm SiO_2, 0.1 μm Si_3N_4) are needed as a diffusion barrier between Si and the films to be tested. This layer stack also adjusts the pre-stress of the Si cantilever. SiO_2 was grown by thermal oxidation in a standard tube furnace. Si_3N_4 was deposited on top of the SiO_2 by LPCVD (low pressure chemical vapour deposition). Polymer masks have been used for defining the respective photo-resist structures for opening the SiO_2 and Si_3N_4 layers by reactive ion etching. The structures were aligned in the [1 0 0] direction in order to achieve cantilevers with perpendicular sidewalls. The cantilevers were fabricated by anisotropic etching of the single crystalline Si substrate in KOH solution (20%, 80 °C), where the SiO_2 and Si_3N_4 layers serve as etch masks. The thickness of the cantilevers can be adjusted by the etch time to a defined value (typically 100 μm). The low thickness allows high curvature changes of the film/cantilever combinations due to hydrogen-induced stress, and thus, a good measurement signal. By using single crystalline Si and the described fabrication process the resulting cantilevers in the array are very uniform with respect to thickness (±3%) and mechanical properties. Fig. 2 shows a 24-cantilever-array, in which the lateral dimensions of the cantilevers are 2 mm × 15 mm with a separation distance of 0.5 mm. Potential hydrogen storage materials are deposited as thin films on top of the cantilevers (Section 3).

2.3. Gas phase hydrogenation screening apparatus

The system designed for screening of hydrogen storage materials in form of thin films is shown in Fig. 3a. The test chamber can be used under vacuum (0.1 Pa) or with hydrogen (p_{H_2}: 0.105 to 5.1 MPa). The automated pressure regulation system has two pressure ranges due to accuracy reasons (0.105–0.6 MPa, accuracy: 1 kPa, and 0.6–5.1 MPa, accuracy: 10 kPa). The pressure can be varied accordingly. At a fixed pressure, the variation of p_{H_2} is typically less than 1%. The purity of the hydrogen gas used is 99.999%. The temperature in the chamber can be varied in steps or continuously from 20 °C to 450 °C. Up to 16 cantilevers can be measured simultaneously (Fig. 2). This is achieved by using a laser diode with an optical arrangement which splits the laser beam into parallel lines. The laser is positioned in such a way that the lines are projected through a 50 mm diameter window on the cantilevers, orthogonally to the long axis of the cantilevers (Fig. 3b). Each cantilever reflects at least two of the lines. The individual reflections are projected on a semitransparent screen and are recorded by a CCD camera at programmable

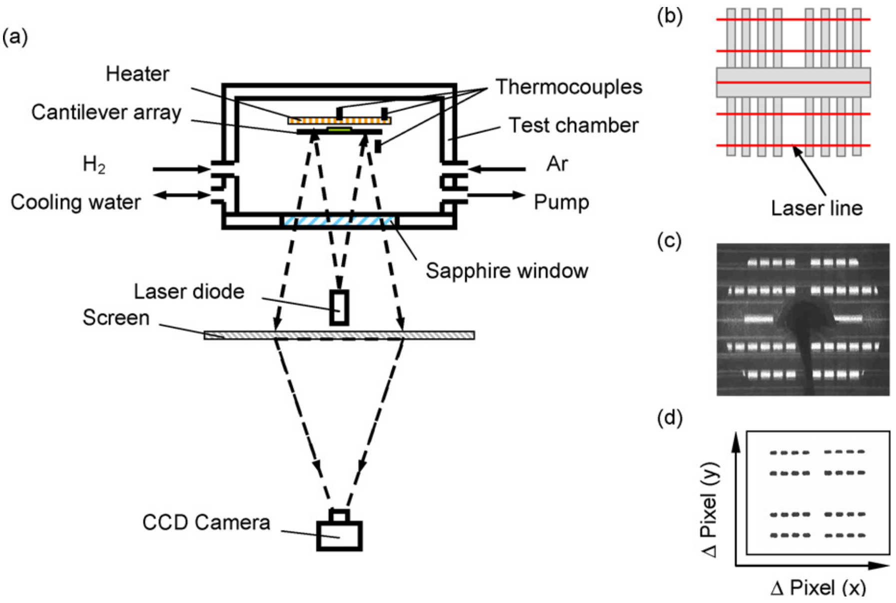

Fig. 3. Set-up for screening hydrogen storage properties in thin films: (a) schematic of the gas phase apparatus, (b) schematic of laser lines projected on cantilevers, (c) CCD camera picture of laser reflections from the cantilevers on the screen and (d) software-processed picture for pixel position determination.

Table 1
Sputter conditions for the investigated thin films (target–substrate distance: 195 mm)

Material (purity of target)	Function of the layer	Sputter conditions		Deposition rate (nm/s)
		Power	Pressure (Pa)	
Pd (99.99%)	Cap layer of Cr_Pd_Pd combinations	300 W RF	0.133	0.29
Pd (99.99%)	Hydrogen storage material of Cr_Pd_Pd combinations	200 W RF	2.66	0.1
Cr (99.99%)	Adhesion layer of Cr_Pd_Pd combinations	200 W RF	0.665	0.09
Pd (99.99%)	Cap layer of Fe_Ti_Pd and Fe_Mg_Pd combinations	27 W DC	0.665	0.13
Ti (99.99%)	Hydrogen storage material of Fe_Ti_Pd combinations	150 W DC	0.665	0.09
Mg (99.95%)	Hydrogen storage material of Fe_Mg_Pd combinations	100 W RF	0.133	0.14
Fe (99.99%)	Adhesion layer of Fe_Ti_Pd and Fe_Mg_Pd combinations	75 W DC	0.665	0.07

time intervals (Fig. 3c). The reflections are then transformed into pixel positions (Fig. 3d) using custom-programmed image analysis software (LabVIEW). The curvature changes of the cantilevers lead to movements of the reflected spots on the screen (measured in Δpixel). Tracking of the positions of points from each cantilever as a function of time gives a measurement of the hydrogen- and/or temperature-induced curvature changes.

3. Experimental

The materials chosen to validate the opto-mechanical screening method are Pd, Mg, and Ti, because of their well-known hydrogenation characteristics [28,29]. Pd was additionally used as the cap layer material, preventing oxidation of Ti- or Mg-based materials and catalytically promoting the dissociation of H_2 on the surface. An adhesion layer between the thin film of interest and the substrate is generally needed in order to avoid delamination of the film upon hydrogenation. However, typical adhesion layer materials like Cr and Ti also form hydrides. Therefore, well-adhering materials which form no hydrides, or do so only under extreme conditions (e.g., Fe) should be used. Contributions of adhesion and cap layers to the stress evolution during hydrogen sorption and desorption have to be considered. For this purpose the combinatorial approach and the deposition of different thin films on selected areas of the substrate was used. By shadow masking, it is possible to deposit thin films in specified locations. In a typical design of the cantilever library, several cantilever positions are reserved for (a) reference (no coating), (b) deposition of only cap and adhesion layer and (c) deposition of the materials of interest (Fig. 2).

All thin films for hydrogen storage were produced by magnetron sputtering using a custom-designed UHV system (DCA, Finland). Elemental targets (100 mm diameter) were used for sputtering in Ar without heating. In order to deposit thin films of selected compositions only in specific locations, stainless steel and silicon shadow masks were used. These masks can be placed, removed or rotated without breaking vacuum in a special mask change chamber of the deposition system. Fe or Cr was used as adhesion layer (~5 nm). The thickness of the Pd cap layer is ~10 nm. Sputter conditions are summarized in Table 1. Film thicknesses were determined by measuring steps with a stylus profilometer (Tencor P10).

4. Results and discussion

Hydrogenation experiments were performed in the above described apparatus under isobaric or isothermal conditions. Here, results of isothermal measurements at room temperature (RT) are presented.

4.1. Simultaneous measurement of thin film/cantilever combinations in hydrogen gas atmosphere at RT

Fig. 4 shows results from simultaneous measurements of a cantilever array. All cantilevers (except reference cantilevers, Fig. 2) were coated with a 5 nm Fe adhesion layer. Then 80 nm Ti was deposited on one quadrant and 80 nm Mg on another. All coated cantilevers were covered with a 10 nm Pd cap layer. The hydrogen storage screening apparatus was first evacuated to a vacuum of ~0.1 Pa; then p_{H_2} was set to 0.105 MPa. The

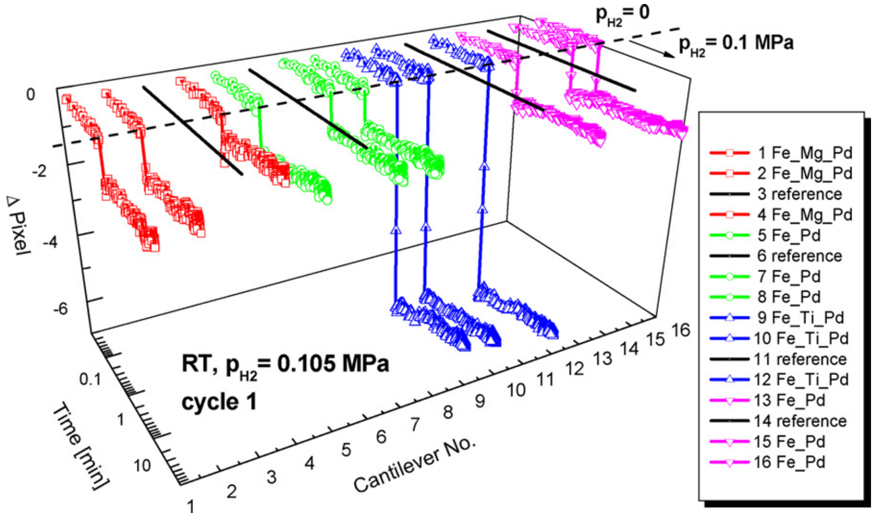

Fig. 4. Results from the simultaneous measurement of hydrogenation of 16 thin film/cantilever combinations ($Si/SiO_2/Si_3N_4$/5 nm Fe/x nm metal/10 nm Pd) at RT; 12 cantilevers are coated as indicated, 4 uncoated as reference.

simultaneously measured movements of the reflected spots from 16 film/cantilever combinations on the screen (Δpixel, Fig. 3) upon hydrogenation (after ∼90 s measurement time) is shown in Fig. 4. Measured signals from the reference cantilevers were subtracted from the signals of neighbouring coated cantilevers, in order to compensate possible movements of the Si wafer. As no other parameter except p_{H_2} is varied, the observed pixel movements (due to curvature changes) can be assigned to the hydrogenation of the thin films. All cantilevers with identical coating exhibit similar responses. The cantilevers with Fe_Ti_Pd coating show the largest curvature changes upon hydrogenation at $p_{H_2} = 0.105$ MPa. The Fe_Mg_Pd cantilevers show similar deflections compared to the Fe_Pd cantilevers. This is attributed to the Pd cap layer, since Mg generally does not absorb hydrogen at RT. The results show that the method allows to distinguish thin films which take up hydrogen at given conditions from films which do not.

4.2. Gas phase hydrogenation of Pd thin film/cantilever combinations at RT

Fig. 5 shows the stress change Δσ of a cantilever (coated with 40 nm Pd, 5 nm Cr adhesion layer, 10 nm Pd cap layer) upon hydrogenation and dehydrogenation at RT. The experiments started from a vacuum of about 0.1 Pa (Fig. 5a). Then p_{H_2} was set to 0.105 MPa and held constant for a given time. Finally p_{H_2} was set to zero and the chamber was purged with Ar for ∼10 s and then evacuated (Fig. 5b). Upon exposing the film to the hydrogen pressure, the compressive stress associated with hydrogenation of Pd increased rapidly to a maximum. Again, as no other parameter except p_{H_2} was varied upon hydrogenation, the observed stress changes can be assigned to the hydrogenation of the thin film. At constant p_{H_2}, the stress relaxes. It can be observed that the first hydrogenation cycle (Fig. 5a) is clearly different from the following cycles: for the first cycle the compressive stress associated with hydrogenation of Pd increased rapidly to a maximum of $\Delta\sigma = -0.98$ GPa within ∼6 s. For the following hydrogenation cycles the behaviour is similar, but the maximum stress changes are higher (∼1.2 GPa) and were reached within ∼72 s after exposing the films to $p_{H_2} = 0.105$ MPa. Fig. 5b shows the complete hydrogenation/dehydrogenation behaviour of the Pd film in the second cycle. During evacuation the compressive stress decreases first very quickly and then gradually to zero. This behaviour might be due to the phase transformation of Pd upon dehydrogenation.

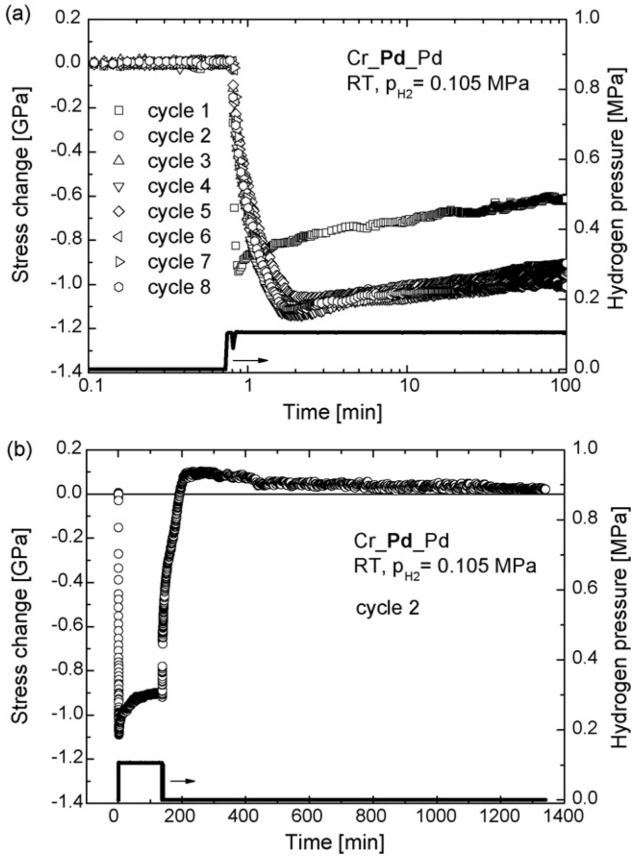

Fig. 5. Stress change due to hydrogenation in the isothermal phase experiments (0.105 MPa, RT) of a Si/SiO_2/Si_3N_4/5 nm Cr/40 nm Pd/10 nm Pd thin film/cantilever combination: (a) repeated hydrogenations and (b) hydrogenation and dehydrogenation.

5. Conclusions and outlook

It has been shown that the new cantilever-based opto-mechanical method is suitable for high-throughput measurements (screening) of the hydrogenation and dehydrogenation properties of thin film/cantilever combinations. The method is feasible for a broad range of materials, as the effect of a volume change associated with hydrogenation is generally encountered in hydrogen storage materials. The results obtained with elemental thin films illustrate the functionality of the method. Next materials to be investigated will be in promising Mg-based systems, prepared in the form of thin film composition spread materials libraries (cantilever arrays).

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