Stress development and adhesion in hydrogenated nano-columnar Pd and Pd/Ti ultra-thin films

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Abstract. Stress development upon hydrogenation of about 100 nm thick palladium layers on thermally oxidized silicon wafers with and without an intermediate Ti layer is studied. Stress developed is investigated by in-situ XRD in H_2/N_2 (hydrogenation) and N_2 (dehydrogenation) gas at RT. The method adopted to measure residual stress involved specimen omega- (ω) and psi- (ψ) tilting, on two different diffractometer geometries (focusing and parallel). For the stress analysis, the presence of intrinsic elastic anisotropy of the film is considered. Upon hydrogenation α-Pd transformation to β-$PdH_{0.6}$ occurs and because of the constrained in-plane expansion a large compressive stress develops. Scanning electron microscopy shows that films with a Ti intermediate layer adhere better to the substrate upon hydrogen cycling, whereas, pure Pd film start cracking and buckling.

1. Introduction

Thin Pd films are of interest as hydrogen separation membranes [1], but high mechanical stresses between a film and its substrate often lead to film detachment and subsequent failure in thin films [2]. By hydrogen loading of Pd film that is clamped to a substrate, high in-plane stresses up to several MPa develop due to volume change. These stresses are high enough to detach films from their substrate, rendering such films of low industrial use [3]. The exact knowledge of the magnitude of the residual stress state is of great technological importance because stresses can be detrimental for the performance of thin film. The technique commonly used for these measurements include X-ray diffraction (XRD). Particularly when using focusing optics for the XRD stress analysis it is important to be aware of line broadening and line shift, as the method is sensitive to alignment errors, unlike parallel beam optics. Hence corrections are needed for reliable stress results [4]. The components of the mechanical stresses are deduced using $\sin^2\psi$-method employing suitable x-ray elastic constants (XEC's) [5]. For thin films, which are (intrinsically) elastically anisotropic, the XEC's differ for various *hkl* reflections and are dependent on single-crystal elastic constants, grain-interaction model and on the crystallographic texture [6,7,8]. In this paper, in-situ and ex-situ hydrogenation stress analysis of Pd films is performed in order to expand the application of nano-columnar Pd thin film to H_2 gas purification and sensing.

2. Experimental

The nanostructured thin Pd films with and without Ti intermediate layer were prepared by magnetron sputtering. Films were sputtered on an oxidized Si single crystal wafer substrate rotating at a uniform rate during the deposition. Sputtering was performed at RT in Volmer-Weber growth mode to achieve loose columnar morphology. The thicknesses of the Pd layer were set to ~100 nm and ~3 nm for Ti layer as estimated by weighing and later confirmed by transmission electron microscopy (TEM) while examining film morphology. X-ray diffraction measurements were carried out using two types of systems (*i*) Bruker-AXS D5005 diffractometer in *Bragg-Brentano focusing geometry* (CuKα), equipped with closed MRI High Temperature (HT) chamber; further called *HT system* for in-situ measurements, and (*ii*) Bruker D8 diffractometer in *parallel beam*

geometry (CoKα), equipped with Huber Eulerian Cradle; further called *PSI system* for ex-situ measurements.

2.1. In-situ ω-tilt stress measurement during Pd phase transformation

Hydrogen cycling of Pd and Pd/Ti films was done during 20 slow Loading/Deloading (L/D) cycles in closed MRI HT chamber, at RT in 1 atm of H_2N_2 and N_2 gas atmosphere respectively. Continuous short 2 min scans were made until complete L/D was achieved at each cycle. Change in Pd film surface morphology after cycling was characterized using scanning electron microscopy (SEM).

In-situ stress measurement was done on HT system, for loaded/deloaded film specimens. During 20 cycles of hydrogen L/D; stress developed in Pd and Pd/Ti films was measured after 1st, 5th, 10th, 15th and 20th -L/D cycles for a single specimen. In-plane (de)-hydrogenation stresses in Pd films, were measured by applying ω-tilt for the Pd-α and Pd-β -{331} and {420} reflections. Positive ω-tilt was applied in the range of 0º- 45º in step mode ($\sin^2\psi$ 0 - 0.5). The defocusing correction was determined using stress-free Palladium powder, for which the stress-free state has been confirmed on the PSI system. Due to the alignment errors in the focusing geometry pseudo-stresses are observed even in stress-free Pd powder. For collecting reliable XRD data, the peak profile statistical accuracy was improved by using adequate irradiated specimen volume and increasing counting time.

2.2. Ex-situ ψ-tilt stress measurement after hydrogen cycling experiment

Pd and Pd/Ti specimens after hydrogen L/D cycling were used for ex-situ stress measurement on the PSI-system. Step scans were performed over a 2θ-range of 96º-104º for the Pd-{311} reflection. Data was collected at six tilt angles ($\sin^2\psi$ 0 - 0.50, steps of 0.10) for a fixed sample orientation (at $\phi = 90º$).

Stress analysis is performed using the $\sin^2\psi$ technique. All the data evaluation was done with the programs Bruker EVA and PANalytical X'Pert Stress Plus [9]. Diffraction patterns from ω-tilt measurements were evaluated by fitting with different peak fitting methods: Parabola, Profile shape function, Centered Center of gravity and mix fit, in order to obtain accurate peak position. Absorption/transparency correction, background subtraction and Kα2-stripping, as intensity corrections were applied to the measured data. The possible alignment corrections were made using stress-free Pd powder, on the raw diffraction data of ω-tilt and ψ -tilt measurements for the stress analysis of (de)-hydrogenated Pd films. The lattice spacing d_ψ was then calculated and plotted as a function of $\sin^2\psi$ to deduce in-plane stress in the Pd films.
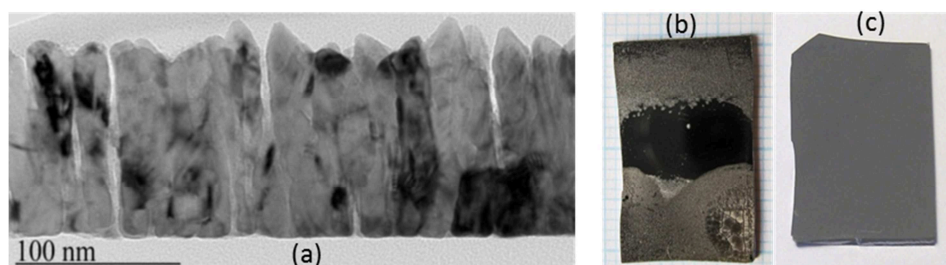
3. Results and Discussion

Figure 1. *(a) TEM bright field image of as-sputtered Pd thin film. Camera picture of specimens (b) Pd film and (c) Pd/Ti film, after 20 H L/D cycles. Pd film has buckled edges with a small flat cracked area in the center and Pd/Ti film remained in as-sputtered condition even after 20 H-L/D cycles.*

Based on the Pd film deposition parameters and from TEM bright field images (Fig. 1a), Pd films show a classic zone-3 morphology characterized by loosely held columnar grains. XRD patterns revealed that films have {111} preferred orientation. After 20 cycles of hydrogen L/D the Pd films

were found partly buckled, starting from edges and growing towards the center (Fig. 1b), whereas, Pd/Ti films remained nicely intact as in as-sputtered condition (Fig. 1c). The observed pseudo-stress in a stress-free reference Pd powder, as a result of the tilt-dependent peak shifts originating from defocusing and specimen displacement errors, from ω-tilt measurements, are listed in Table 1.

Table 1. *Pseudo-stress measured in stress-free Pd powder by* ω-*tilt and* ψ-*tilt stress methods. For Pd-{311}, {331} and {420} reflections peak positions are deduced by four different peak fitting methods.*

ω -tilt Stress (MPa)	Pseudo-stress in stress-free Pd powder			
	Centered Center of Gravity	Parabola	Profile shape function	Mixed
Pd-{331}	-31.9±5.7	-36.2±4.6	-30.9±5.0	-33.3±2.7
Pd-{420}	-13.8±4.9	-19.2±4.3	-14.6±2.0	-13.9±4.7
ψ -tilt Stress				
Pd-{311}	-0.9±0.9	-0.1±1.5	-1.2±0.9	-1.3±0.7

3.1. Stress analysis: Sin²ψ method

The determination of compressive and tensile stresses and strain-free lattice parameters (d_0 and $sin^2\psi_0$) has been carried out using the traditional $Sin^2\psi$-method. This method in principal allows the full assessment of the mechanical stress state of a sample from the spacing of one or more families of lattice *hkl* planes measured. In-plane stress for the case of planar, rotationally symmetric biaxial state of stress ($\sigma_{11} = \sigma_{22} = \sigma$), was calculated from Eq. 1 [5,7].

$$\varepsilon_\psi^{hkl} = \frac{d_\psi^{hkl} - d_0^{hkl}}{d_0^{hkl}}; \ \ \varepsilon_\psi^{hkl} = (2S_1^{hkl} + 1/2 \, S_2^{hkl} sin^2\psi)\sigma \tag{1}$$

For the residual stress analysis involving particular *hkl* reflections, the measured lattice strain is not a direct measure of the average mechanical strain of all crystallites, therefore, x-ray diffraction data are highly susceptible to the elastic anisotropy. This can be taken into account by using the so-called grain-interaction models that describe the distribution of stresses and strains over the crystallographically differently oriented crystallites in the specimen [7,10]. Elastic constants of Pd change with H content in the lattice, which results in change of XEC's of Pd loaded with hydrogen. Suitable XEC's ($^{hkl}S_1$ and $\frac{1}{2}^{hkl}S_2$) were calculated using widely applied grain-interaction models: Voigt, Reuss, and Hill's weighted average, from single-crystal elastic constants of Pd and PdH$_{0.6}$ at 300 K [11].

For a Pd film clamped onto a substrate, only in-plane grain interactions are expected, as compressive forces due to the hydrogenation results in a biaxial state of stress exerted by the substrate. The surface of the film is free, so there is no stress built-up in the perpendicular direction. Hence, the (de)-hydrogenation stresses in these Pd films were estimated by using Hill's weighted average grain-interaction model, which is the arithmetic average of x-ray and macroscopic elastic constants as calculated with the Reuss and the Voigt grain-interaction model.
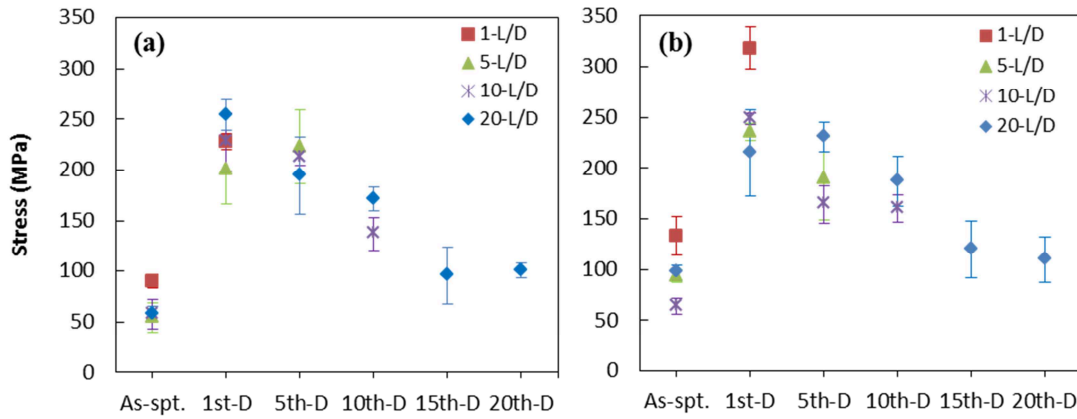
Figure 2. *Residual stress vs number of deloading cycles. Peak positions are evaluated by fitting using (a) Centered Center of Gravity and (b) Parabola method for ω-stress analysis. A legend indicating four H-L/D experiments performed on different Pd film specimens under similar setup and conditions.*

Various hydrogen L/D experiments with different test setups were performed to test applicability of ω -tilt method for reliable in-situ stress results. In-situ deloading stresses measured during four experiments using every time different Pd film specimens are collected in Fig. 2, showing 1, 5, 10, and 20 -L/D cycles performed at RT; for comparison peak positions were determined with the Centered Center of Gravity (Fig. 2a) and the Parabola (Fig. 2b) method. For both fitting methods only a fraction of the upper portion of the peak was included, so as to avoid the region of overlap between the Pd-{331} and {420} peaks. However, the peak position will vary as a result of defocusing as the tilt-angle is changing during the course of stress measurement. After subtracting the pseudo-stress (Table 1) from the measured stress, the possible defocusing error was corrected for and thus the calculated stress for different L/D experiments lies within the error limits (corresponding to the counting-statistical error resulting from peak fitting) (Fig. 2). For a satisfactory conclusion about the measured ω -stress results, ex-situ residual stress measurements were performed using the PSI-system with parallel beam optics. Results from both the methods are compared and discussed further.
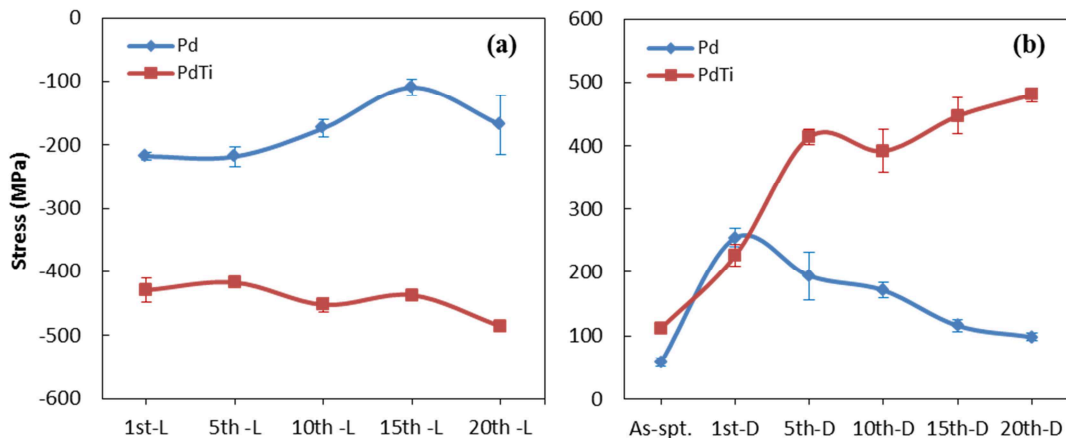

Figure 3. *In-situ stress measurements of Pd and Pd/Ti thin films for (a) 20 H-loading cycles and (b) 20 H-deloading cycles, in-situ stress performed at 1st, 5th, 10th, 15th and 20th L/D cycle. Peak fitting using Centered Center of Gravity method.*
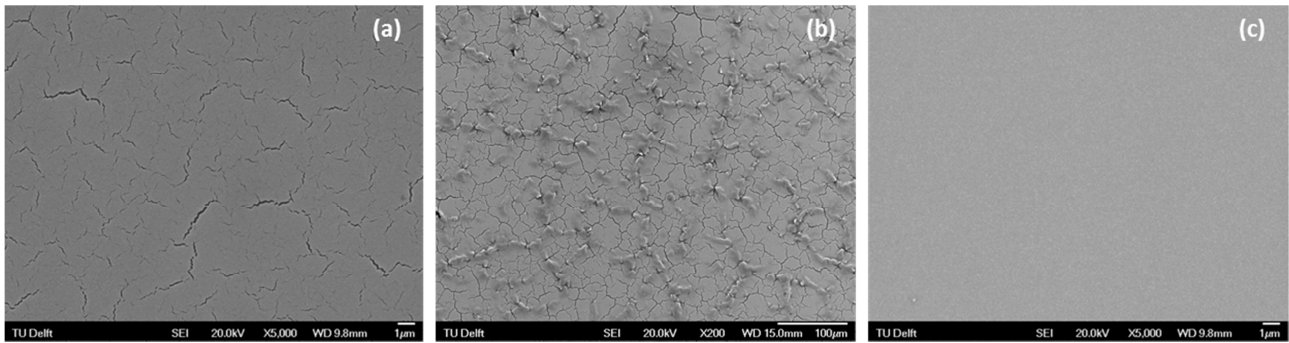
Figure 4. *SEM micrographs: (a) Pd film after 5 L/D cycles, showing propagating microcracks, (b) Pd film after 20 L/D cycles, showing both buckled and microcraked area, (c) Pd/Ti film without any microcracks or buckles even after 20 L/D cycles, remained in as-sputtered condition.*

In thin Pd films adhered to the substrate the $\alpha \leftrightarrow \beta$ phase transition induces in-plane compressive forces during (de)-hydrogenation [3]. In-situ stress measured during hydrogen L/D cycles for Pd and Pd/Ti thin films are plotted in Fig.3. The difference of compressive stress developed in Pd and Pd/Ti films upon H loading is almost of factor 2. The deloading-stress kept declining as more and more L/D cycles were performed; this stress relaxation is due to film cracking/buckling (Fig. 4). Buckles start spreading from the free end of the film, growing toward the center (Fig. 1b). For Pd/Ti films the deloading tensile stress was found increasing with increase in H-L/D cycles, because the Ti adhesive layer constrained free expansion during hydrogenation. Fig. 5 shows the evolution of the deloading residual stress in Pd and Pd/Ti films for three reflections in both in-situ and ex-situ conditions. There is an increase in the residual stress from the as-sputtered state to that after 1st H-L/D cycle and decrease further up to 20 cycles for Pd film (Fig. 3b and 5a) occurs. For Pd/Ti films the residual stress kept increasing after hydrogen cycling compared to the as-sputtered condition (Fig. 3b and 5b). The stress followed by in-situ residual stress on Pd-{331} and Pd-{420} reflections is found to decrease for Pd film and increase for Pd/Ti film with increasing cycles, and this is in agreement with the more reliable ex-situ stress measured for Pd-{311} reflection in parallel beam configuration.
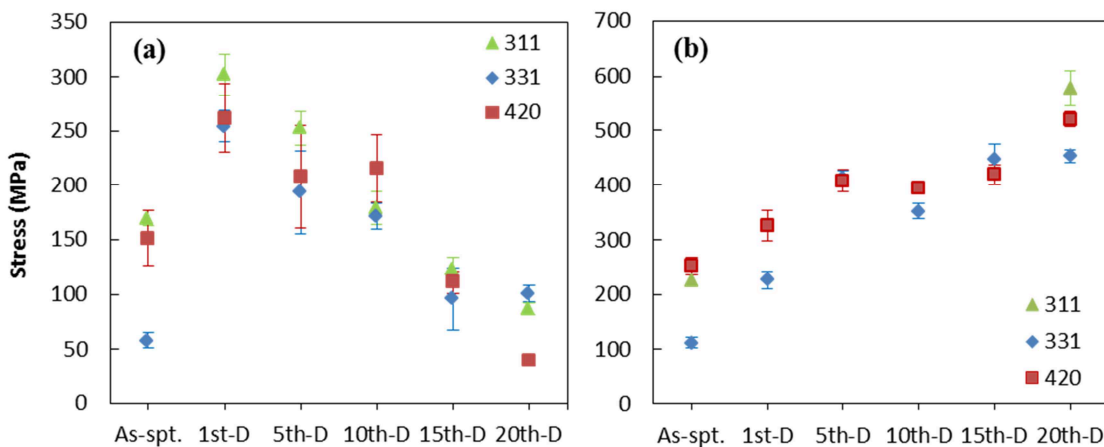

Figure 5. *Comparing residual stress in (a) Pd and (b) Pd/Ti film, after L/D experiments, measured both in-situ (HT-system) for the{331}&{420} reflections and ex-situ (PSI-system) for the Pd-{311} reflection.*

4. Summary

From the work done we can conclude that using the available focusing optics geometry, stress determination by ω-tilt method can be used to estimate the in-situ stress developed in Pd films

during (de)-hydrogenation cycling. In-situ ω-tilt measurement results show similar trends for the Pd film residual stress as shown by ex-situ ψ-tilt measurements, within the estimated error. Alignment corrections for ω-tilt diffraction measurements were made, by performing verification measurements on a stress-free reference Pd-powder. Beside this, the experiments also showed the necessity of a detailed analysis of the in–situ XRD data from the HT system, i.e. appropriate choice of fitting method for obtaining peak positions.

This work also demonstrates that using Ti as an adhesive intermediate layer prevents pure Pd film failure due to α ↔ β phase transitions during hydrogen cycling. The results show that the compressive stress developed in Pd/Ti films is about twice that in the Pd films. It is shown that the stress in the Pd film is released by buckling and that in the Pd/Ti film the adhesive force is higher than the forces required to form buckles or to detach film from the substrate. Thus, a Ti adhesive layer can be used to enhance the lifetime of ultra-thin Pd films during hydrogen cycling.

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