

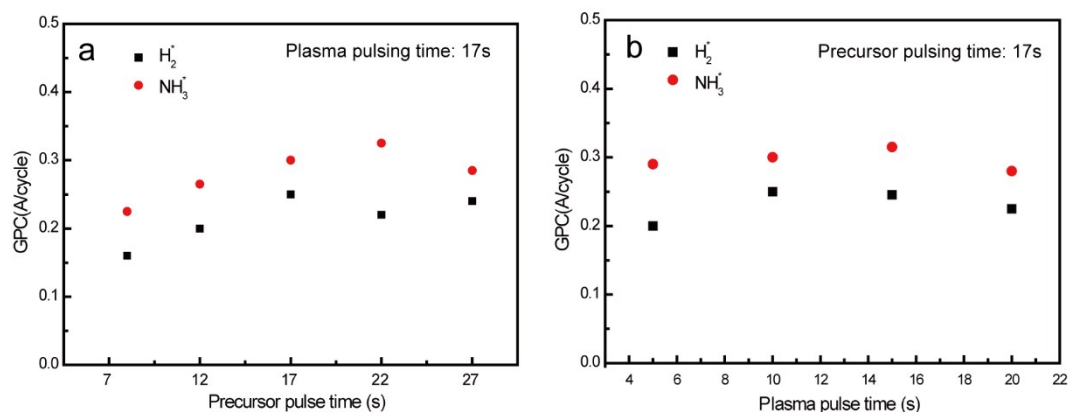
# The co-reactant role during Plasma Enhanced Atomic Layer Deposition of Palladium

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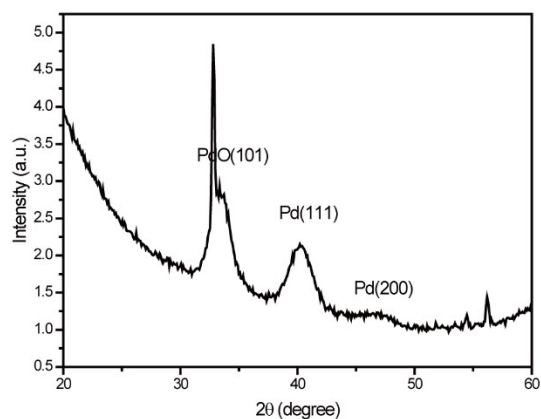
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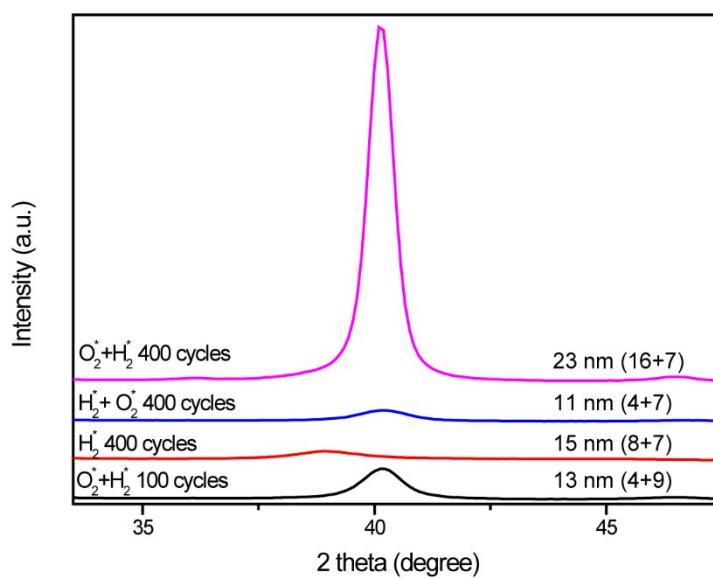
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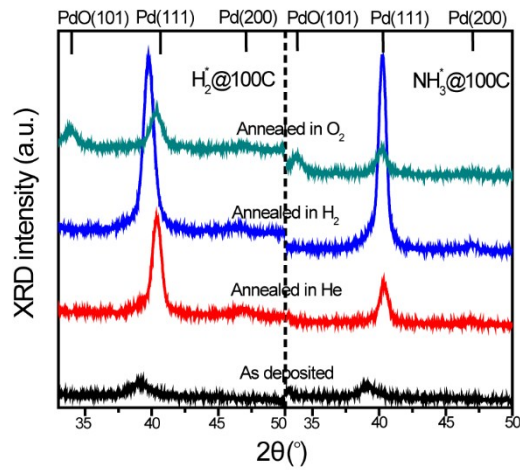
**Figure S.1** Saturation curve of a)precursor: Pd(hfac)<sub>2</sub> exposure and b)reactant: H<sub>2</sub>\* and NH<sub>3</sub>\* exposure as a function of pulsing time at 150 °C.



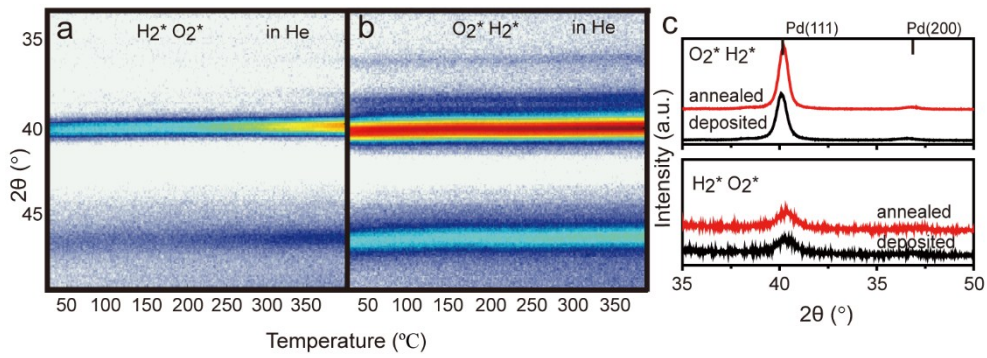
**Figure S.2** XRD patterns of 400cycle Pd ALD with only O<sub>2</sub>\* on sputtered Pd. Except for Pd diffraction peak, it shows a PdO(101) peak. The sharp peak near PdO(101) belongs to Si(200).



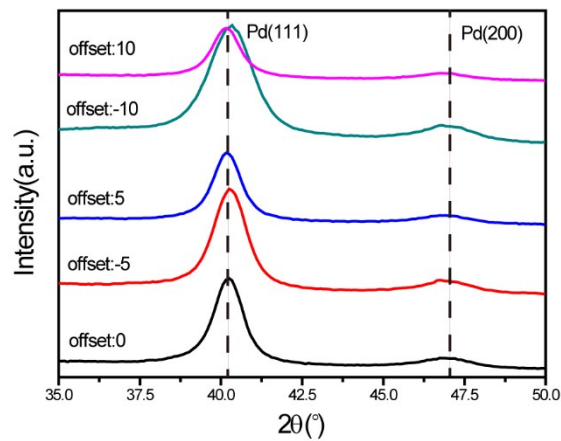
**Figure S.3** XRD pattern of as-deposited Pd thin films by the ALD processes alternating exposures of Pd(hfac)<sub>2</sub> and different plasma and plasma sequences. The approximate thicknesses of Pd films (ALD+sputtered) are marked on the right.



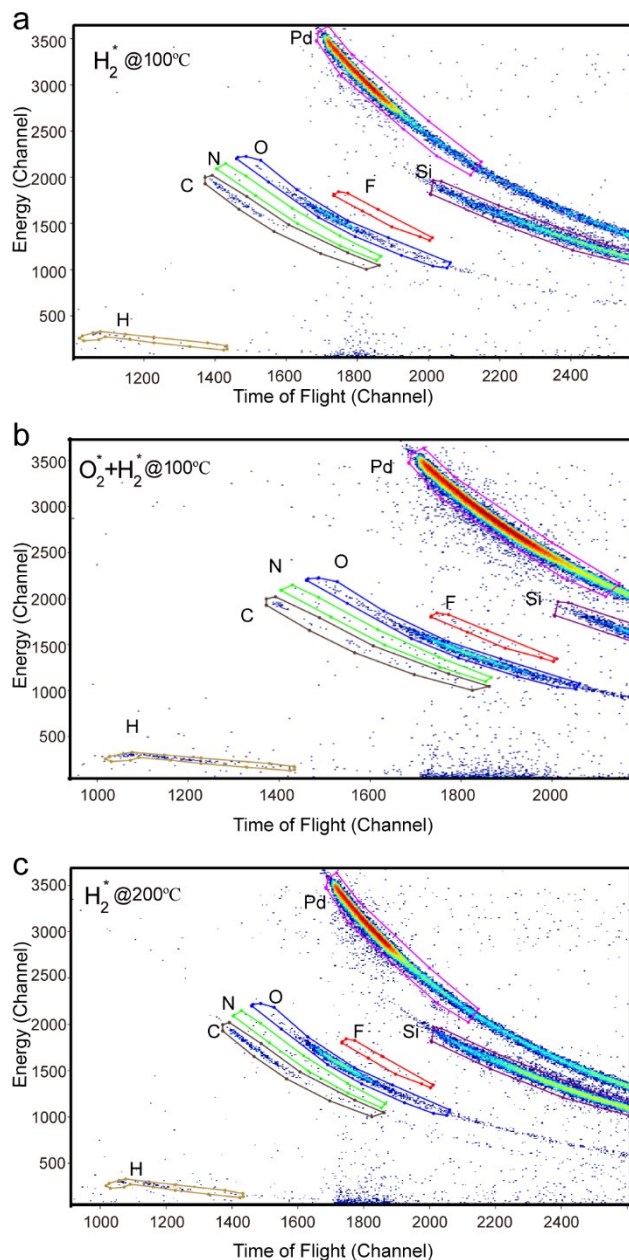
**Figure S.4** XRD patterns of as deposited and annealed Pd films grown with  $H_2^*$  (left) and  $NH_3^*$  (right) at  $100^\circ C$ . The as deposited Pd films were annealed in He, 5%  $H_2$  in He and 5%  $O_2$  in He.



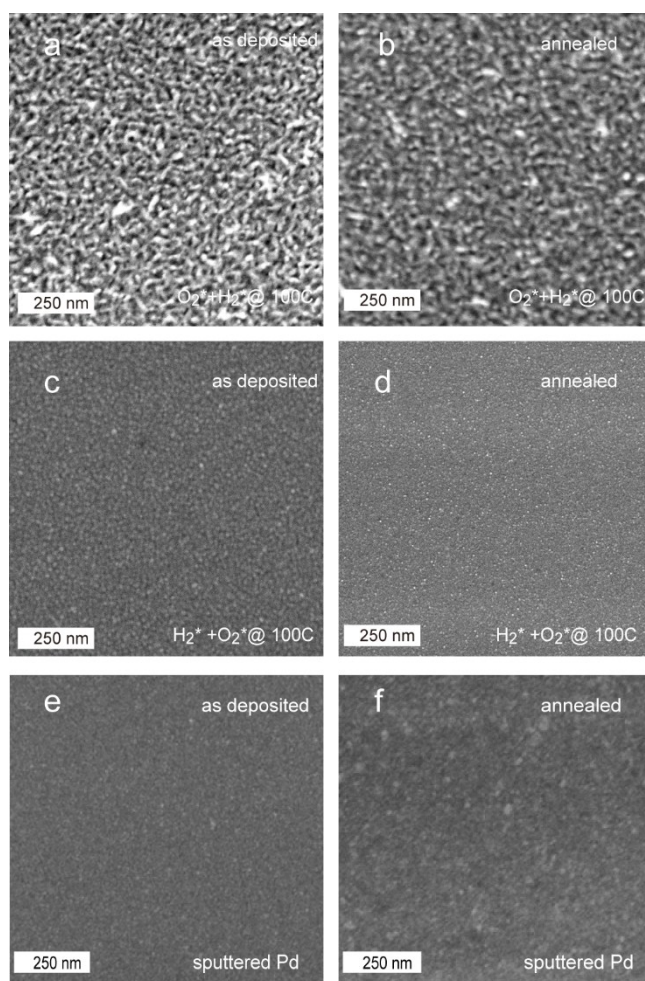
**Figure S.5** In-situ XRD ramp annealing graphs at  $0.2^\circ C/s$  to  $400^\circ C$  for Pd films grown by (a)  $H_2^* + O_2^*$ ; (b)  $O_2^* + H_2^*$  at  $100^\circ C$ . (c) Ex situ XRD patterns of as-deposited and annealed are shown in the right picture.



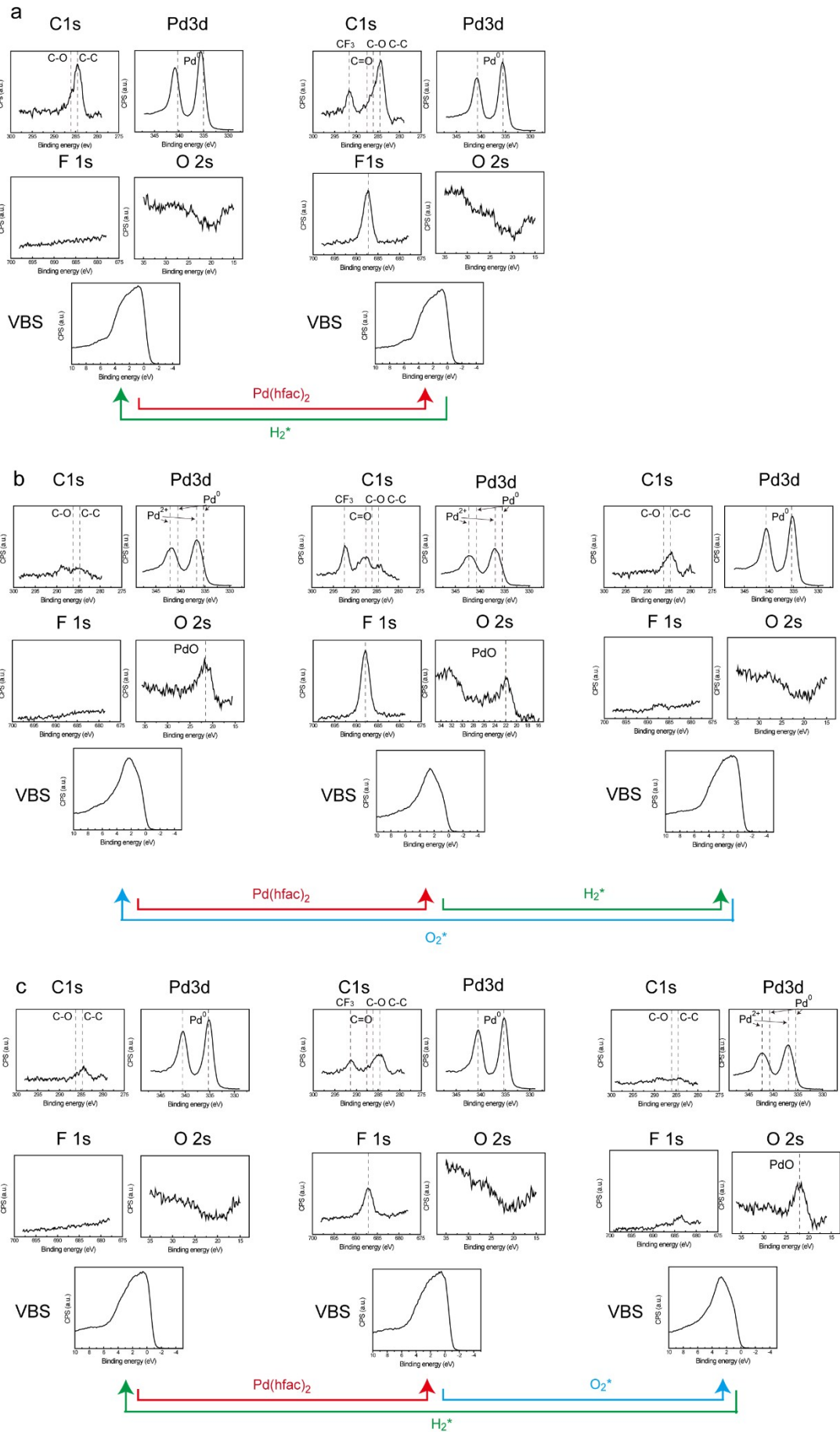
**Figure S.6** XRD patterns of sputtered Pd thin films as seed layers in this work with different offset angles. It shows that seed layers are polycrystalline with the original bulk spacing in the lattice.



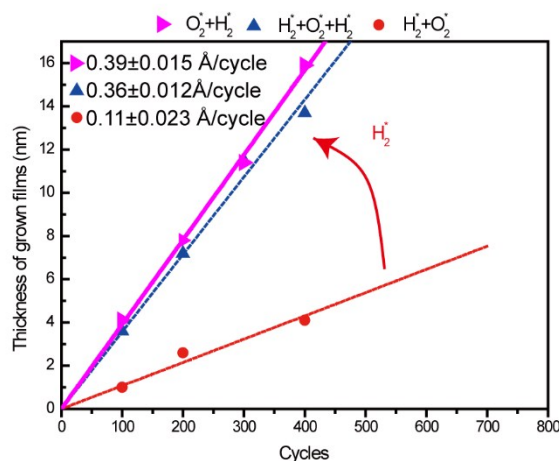
**Figure S.7** ERD spectra of Pd thin films on sputtered Pd seed layers by applying ALD cycles comprising alternating exposures of Pd(hfac)<sub>2</sub> and (a) H<sub>2</sub><sup>+</sup> at 100°C, (b) O<sub>2</sub><sup>+</sup>+H<sub>2</sub><sup>+</sup> at 100°C and (c) H<sub>2</sub><sup>+</sup> at 200°C. The total Pd thicknesses including the sputtered layers are ~ 25 nm for the three samples. Every so called ‘banana curve’ represents a certain element. Banana curves with lower energy and small Time of Flight refers to lower mass elements. Within one banana curve, signals with lower energy and larger Time of Flight indicates the elements deeper in the films. The signals in the drawn contours were integrated to obtain the depth profile in Figure 6.



**Figure S.8** Top view SEM graphs of selected ALD Pd on sputtered Pd: (a) as deposited Pd films grown with  $\text{O}_2^* + \text{H}_2^*$  at  $100^\circ\text{C}$ ; (b) post-annealed samples in He of (a); (c) as-deposited Pd films grown with  $\text{H}_2^* + \text{O}_2^*$  at  $100^\circ\text{C}$ ; (d) post-annealed samples in He of (c). Top view images of (e) as-deposited and (f) annealed sputtered Pd thin films ( $\sim 13$  nm). The annealing was conducted at He atmosphere with a ramping rate of  $0.2^\circ\text{C/s}$  to  $400^\circ\text{C}$ .



**Figure S.9** In vaco XPS data for C 1s, Pd 3d, F 1s, O 2s and valence band after each precursor and plasma exposure for the ALD processes with a)  $\text{H}_2^*$ , b)  $\text{H}_2^*+\text{O}_2^*$  sequence and c)  $\text{O}_2^*+\text{H}_2^*$  sequence. The pass energy for the valence band is 100 eV, while 200 eV for all the other spectra. Pd and C signals are already shown in Figure 8 of the main text but also displayed here for clarity.



**Figure S.10** Grown Pd film thickness on sputtered Pd substrates by alternating Pd(hfac)<sub>2</sub> and different plasmas and plasma sequences at 100°C as a function of the numbers of ALD cycles. The full lines are the linear least-square fits to the data sets. The slopes of these lines are listed in the legend as the GPC of the processes, with an error determined as 3 times the standard error on the slope of the least-squares fits.

### Supplementary Note: Hydriding and dehydriding process monitored by in-situ Ellipsometry

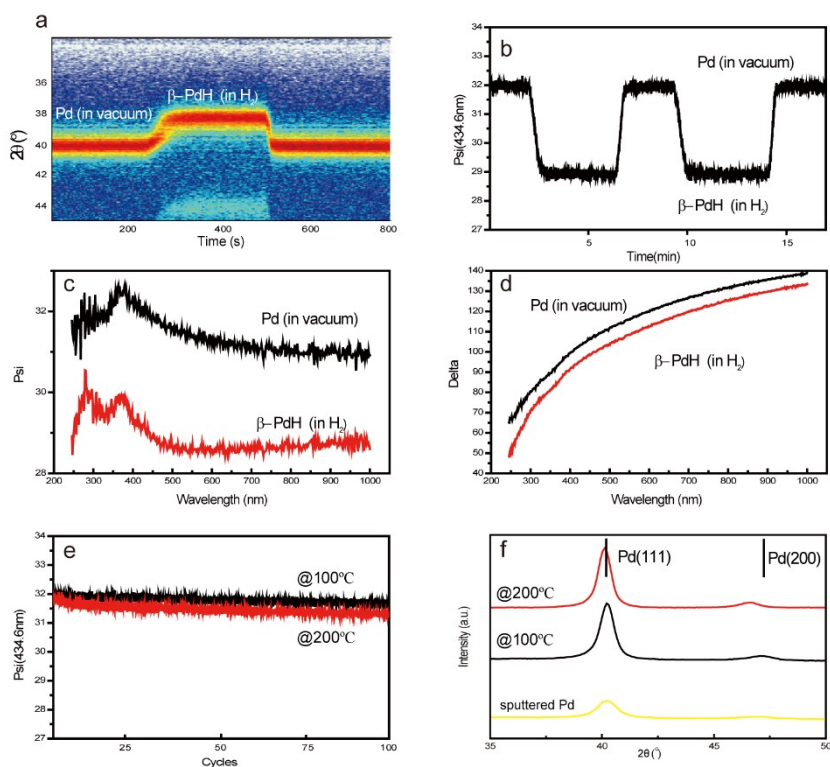
Except for carbon, another well-known impurity giving rise to the shifted diffraction peak is hydrogen. Pd attracts a broad interest in applications as hydrogen sensor and storage for its strong adsorption capacity of hydrogen.<sup>1,2</sup>

Hydrogen occupies the octahedral sites of the fcc crystal structure, expanding the crystal lattice and increasing the lattice constant. Therefore, the diffraction peaks of palladium hydride ( $\text{PdH}_x$ ,  $x \leq 1$ ) shift to smaller  $2\theta$  positions and the degree is related to the amount of hydrogen in the lattice.<sup>3</sup> According to a hydrogen pressure-composition (PC) isotherms study of Pd-H system, the presence of a certain  $\text{H}_2$  partial pressure applied over Pd leads to the formation of  $\text{PdH}_x$  and the opposite dehydriding process occurs when the  $\text{H}_2$  pressure is removed.<sup>4,5</sup> In recent years, new advances were achieved in studying the size dependent kinetics of hydriding and dehydriding of Pd nanostructures.<sup>6,7</sup>  $\text{H}_2^*$  treatment is also reported to possibly form  $\text{PdH}_x$ , which is relevant to the present research of Pd PE-ALD.<sup>8</sup>

To investigate the  $\text{H}_2^*$  treatment effect of Pd for the current ALD experimental conditions, real-time in situ ellipsometry was used to monitor the status of the Pd thin films. First of all, a reference is needed to estimate the ellipsometric constants of Pd and  $\text{PdH}_x$ . In-situ XRD reveals the phase transition of Pd and  $\text{PdH}_x$  at 21 °C when 50 mbar  $\text{H}_2$  partial pressure is applied on a 20 nm sputtered Pd thin film. The restitution of the diffraction peak is found when  $\text{H}_2$  is pumped away. The same experiment was repeated in the ALD reactor monitored by in-situ ellipsometry with an even higher  $\text{H}_2$  partial pressure of 200 mbar

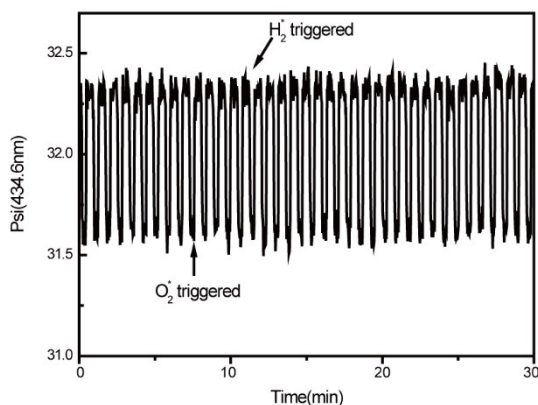
to ascertain the formation of PdH<sub>x</sub>. A reversible change of optical properties ( $\Psi$  for example) is observed with the presence and absence of H<sub>2</sub> atmosphere (**Figure S.11b**). Without changing the atmosphere, the optical properties like ellipsometric  $\Psi$  and  $\Delta$  of Pd or PdH<sub>x</sub> is stable (**Figure S.11 c,d**). In this way, optical parameter evolution acquired by in-situ ellipsometry is used to indicate the hydriding and dehydriding process.

The hydriding process of sputtered Pd was studied during continuous H<sub>2</sub>\* treatments with the same conditions as applied in Pd PE-ALD applied and real-time ellipsometry recorded the evolution of optical properties (**Figure S.11 e**). Unlike a full immersion in H<sub>2</sub> atmosphere, even 100 times 10s H<sub>2</sub>\* treatment (100 W, 1 x 10<sup>-2</sup> mbar) is not able to make a transition from Pd to PdH<sub>x</sub>. Moreover, the XRD patterns do not show the transition of diffraction peak position either (**Figure S.11 f**). Meanwhile, an alternate exposure of H<sub>2</sub>\* and O<sub>2</sub>\* on sputtered Pd shows a slight periodical transition of optical properties, indicating the reduced and oxidized surface status of the Pd surface after these two plasma treatments, verified by in vacuo XPS measurement (**Figure S.12**).



**Figure S.11** Pd and  $\beta$ -PdH as reference for in situ real time ellipsometry measurement: a) phase transition between Pd and  $\beta$ -PdH through exposing 20 nm sputtered Pd to a high H<sub>2</sub> partial pressure, measured by in situ XRD; b) similar experimental conditions as a) performed in the ALD reactor and monitored by in situ real time ellipsometry; c)  $\Psi$  (Psi) and d)  $\Delta$ (Delta) of Pd and  $\beta$ -PdH vs wavelength(nm) measured by in situ ellipsometry; e) real time optical properties of 20 nm sputtered Pd films during 100 H<sub>2</sub>\* pulses at 100°C and 200°C, monitored by in situ ellipsometry; f) XRD patterns of sputtered Pd films before and after H<sub>2</sub>\* treatment at 100°C and 200°C.





**Figure S.12** Optical properties (Psi) evolution of a 20nm sputtered Pd thin film treated with alternating H<sub>2</sub>\* and O<sub>2</sub>\* at 200°C. Psi oscillates within a small window when a different plasma is applied, because of the different surface state after each plasma. The different signal height when using O<sub>2</sub>\* suggests that near surface hydrogen after H<sub>2</sub>\* is removed by O<sub>2</sub>\*.

### Supplementary Reference

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