Supporting Information

Adsorption and reaction mechanisms of direct palladium synthesis by ALD using $Pd(hfac)_2$ and ozone on Si (100) surface

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Methodology

To study the effect of substrates' surface condition on the adsorption and reaction mechanisms of $Pd(hfac)_2$, hydroxylated Si (100) surface at low OH group coverage was constructed.

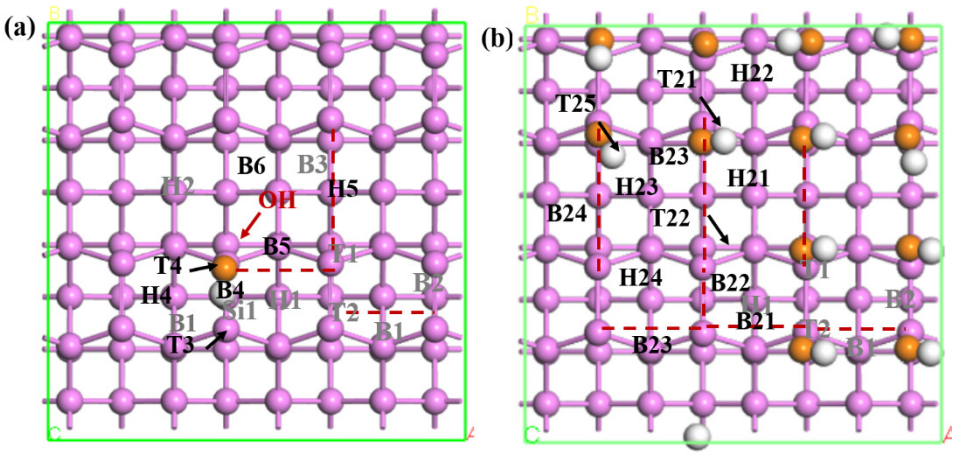

Figure S1 Configurations of (a) 1/16 ML and (b) 3/4 ML OH/Si (100) surface.

An OH group was put on the resulted clean Si (100) surface (1/16 monolayer (ML) OH group coverage, cited as "1/16 ML OH/Si (100)"), and the layers were relaxed. Besides, the optimal adsorption site for the OH group was simulated. Also, fourteen different adsorption sites, including the seven sites mentioned in Figure 1a, were simulated (Figure S1a). To study the effect of OH group coverage on the adsorption of $Pd(hfac)_2$, twelve OH groups were put and optimized on the relaxed clean Si (100) surface (3/4 ML OH group coverage, cited as "3/4 ML OH/Si (100)). Besides, seventeen different adsorption sites, consisting of five sites except for B3 and H2 sites shown in Figure 1a, were calculated (Figure S1b).

Results and discussion

The effect of the substrates' surface conditions

To elucidate the effect of substrates' surface conditions on adsorption and reaction mechanisms of $Pd(hfac)_2$ on Si (100) surface, hydroxylated Si (100) surface was

employed.

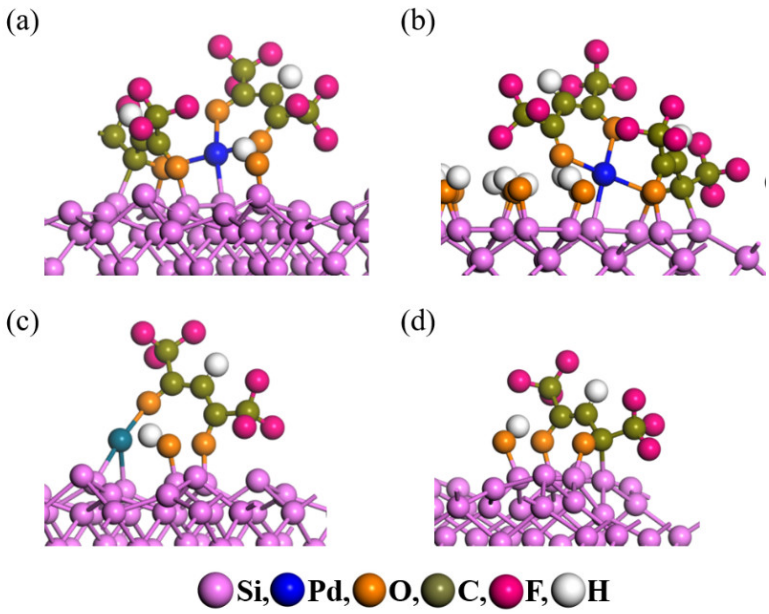

Figure S2 Optimized geometries of different adsorbed species ($Pd(hfac)_2$*(a, b), Pd(hfac)*(c) and hfac*(d)) on (a, c, d) 1/16 ML and (b) 3/4 ML OH/Si (100) surfaces.

Figure S2a and b compare the most stable structures of $Pd(hfac)_2$ adsorption on 1/16 ML and 3/4 ML OH/Si (100) surfaces. As seen in Figure S2a, the most stable structure for the adsorption of $Pd(hfac)_2$ on 1/16 ML OH/Si (100) surface is obtained at B1 site. The adsorption energy is -3.12 eV, indicating that $Pd(hfac)_2$ strongly chemisorbs on 1/16 ML OH/Si (100) surface. With the OH group coverage up to 3/4 ML, the lowest adsorption energy of -3.21 eV is obtained from the initial configuration with the $Pd(hfac)_2$ at B1 site, as illustrated in Figure S2b. The adsorbed $Pd(hfac)_2$ structure on 3/4 ML OH/Si (100) surface is similar to that on 1/16 ML OH/Si (100) surface. Those results indicate that OH group coverage does not significantly affect the structure of the adsorbed $Pd(hfac)_2$ because $Pd(hfac)_2$ prefers to adsorb on the site without OH group. Besides, similar to the case of $Pd(hfac)_2$ adsorption on clean Si (100) surface, $Pd(hfac)_2$ dissociation instead of ligand exchange occurs on hydroxylated Si (100) surface, which differs from the results

shown by Elam et al. [1]. They stated that Hhfac was produced after $Pd(hfac)_2$ adsorption on hydroxylated Al_2O_3 surface. Therefore, the adsorbed OH (cited as "OH*") group has different effects on the $Pd(hfac)_2$ adsorption on different substrate surfaces. Meanwhile, OH group coverage only slightly helps to improve the stability of the adsorption configuration. Hence, 1/16 ML OH/Si (100) is used for our analysis in the following work.

The lowest reaction energy for reaction (1) on 1/16 ML OH/Si (100) is -1.71 eV, similar to that on clean Si(100) surface, which means that $Pd(hfac)_2$* dissociation occurs. Figure S2c and d depict the most stable structures of Pd(hfac) and hfac adsorption on 1/16 ML OH/Si (100) surface respectively, which are similar to those on clean Si (100) surface. Also, the energy of Pd(hfac) adsorption on 1/16 ML OH/Si (100) surface is -4.17 eV, only 0.09 eV lower than that on clean Si (100) surface, indicating that the presence of OH* group does not play a significant role in the movement of Pd(hfac)*. The result is consistent with Lei et al. [2] who reported that the effect of OH* group on the Pd(hfac) adsorption on TiO_2 (110) surface was limited.

In conclusion, the adsorption and dissociation of $Pd(hfac)_2$ on hydroxylated Si (100) surface is similar to those on clean Si (100) surface because OH* group is not the adsorption site of $Pd(hfac)_2$ in the surface reaction. Hence, the effect of the substrates' surface conditions on the growth of palladium is limited, and we can get palladium on hydroxylated and clean Si (100) surfaces at the same preparation temperature theoretically.

References:

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Table S1 showing calculated bond lengths and angles of the $Pd(hfac)_2$ precursor. The atomic labels are referenced from Figure 2.

	Pd-O	O-Pd-O	C1-C2	C2-C3
GGA-PW91	2.00	92.0	1.54	1.39
Experiment[3]	1.97	90.0	1.53	1.39
B3LYP[4]	2.01	92.8	1.54	1.39