Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Determination of growth regimes of Pd nanostructures on c-plane sapphire by the control of deposition amount at different annealing temperature

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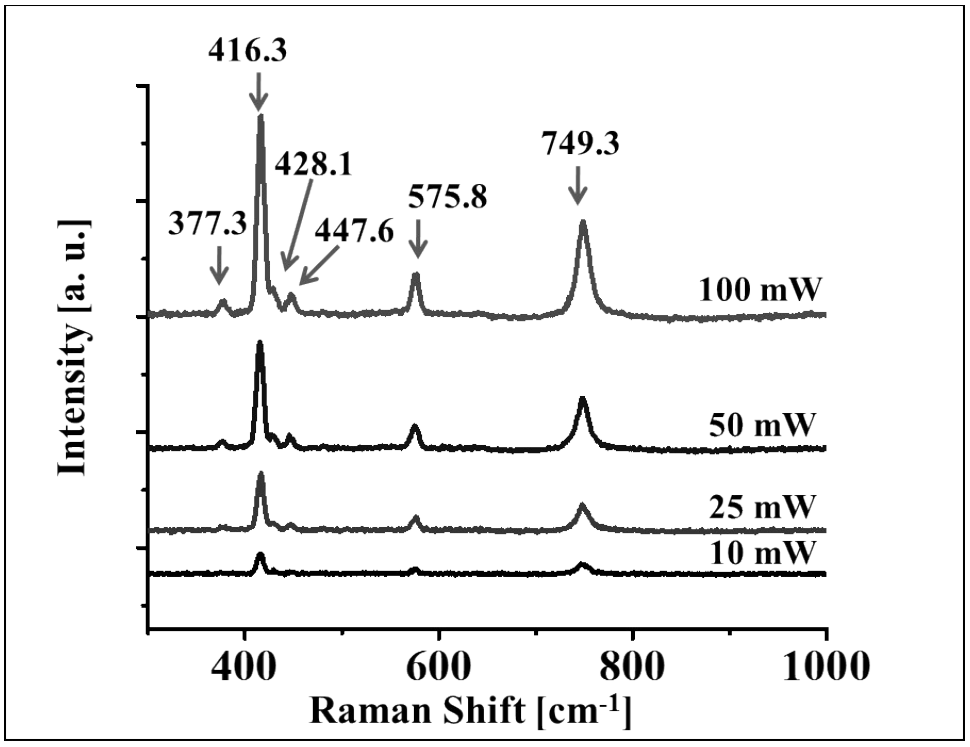

Figure S1: Raman spectra of 430 μm thick bare sapphire (0001) measured at room temperature by the excitation of 532 nm laser. Six active Raman modes from the sapphire (0001) at 377.3, 416.3, 428.1, 447.6, 575.8 and 749.3 cm^{-1} were detected and peak positions are denoted by the arrows. The peak at 416.3 cm^{-1} is due to the A_{1g} vibration mode whereas the others are due to the E_g vibration modes of sapphire. Different power levels were used to obtain the Raman spectra as denoted. Low intensity vibration modes are clearly detected with high power.

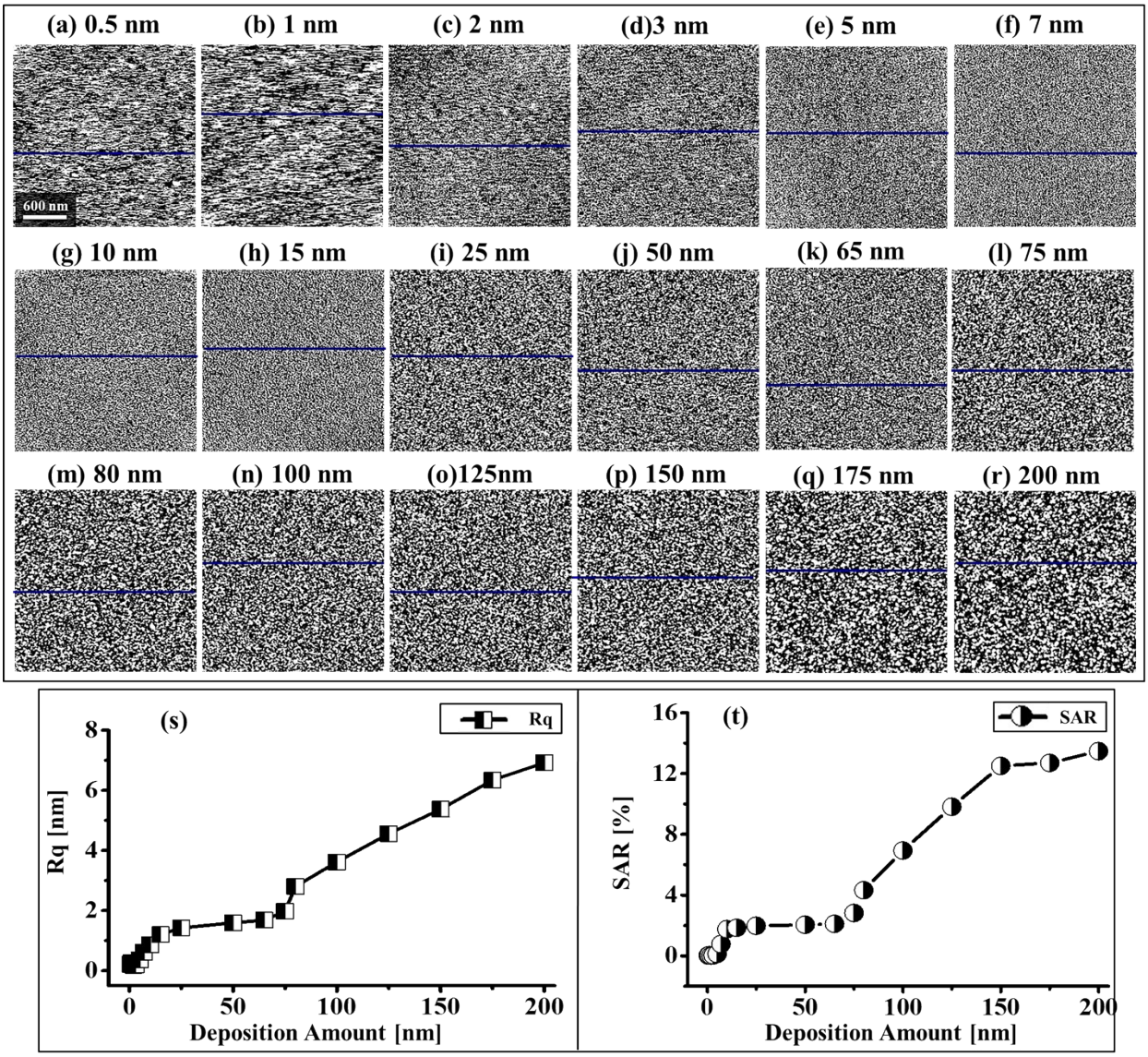

Figure S2: (a) – (r) AFM top-views of 3 × 3 μm^2 showing pre-annealed Pd deposition on sapphire (0001) ranging from 0.5 to 200 nm. (b) RMS roughness (Rq). (c) Surface area ratio (SAR). Generally, the Pd atoms were uniformly distributed and the surface roughness is monotonously increased with the deposition thickness. The specific values of RMS roughness and SAR are listed in table S1.

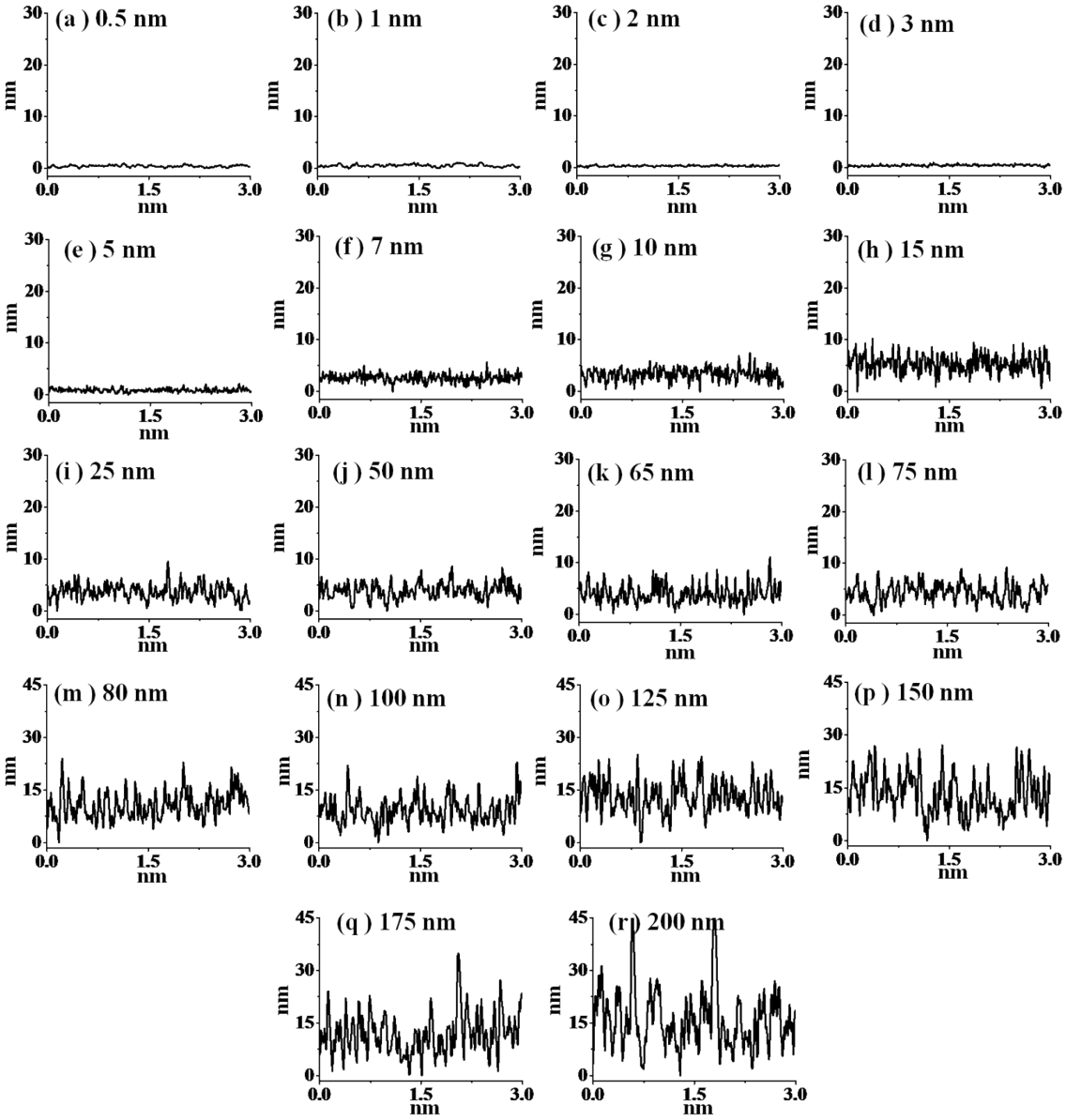

Figure S3: Cross-sectional line profiles of the AFM top-views in Fig. S2. The surface roughness as well as the thickness range is gradually increased as shown by the cross-sectional line profiles.

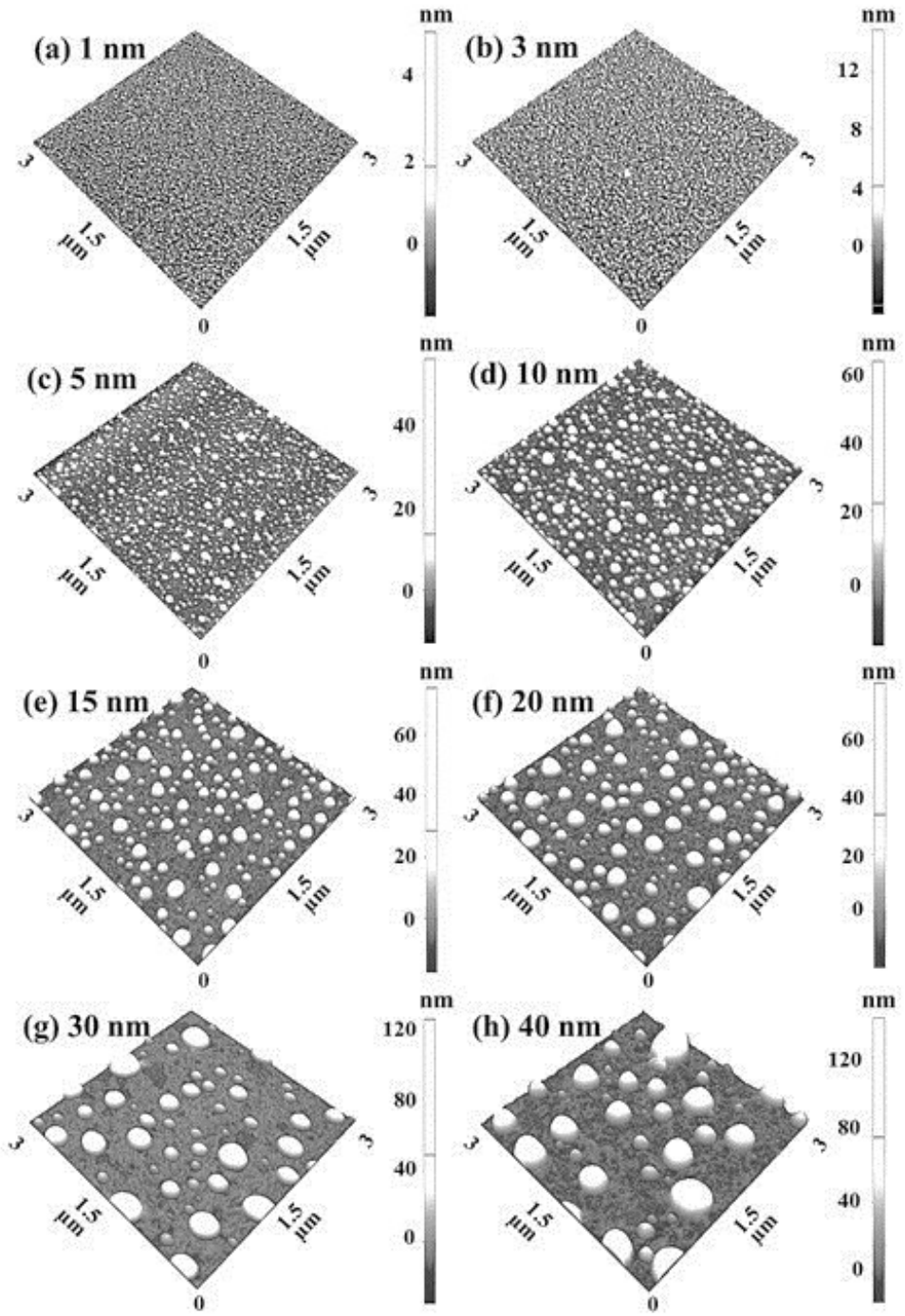

Figure S4: Evolution of round-dome shaped Pd NPs on sapphire at 850 °C for 450s with the variation of the deposition amount from 1 to 40 nm. (a) – (h) 3-D AFM side views of 3 × 3 μm^2. The corresponding color scale bars represent the height information.

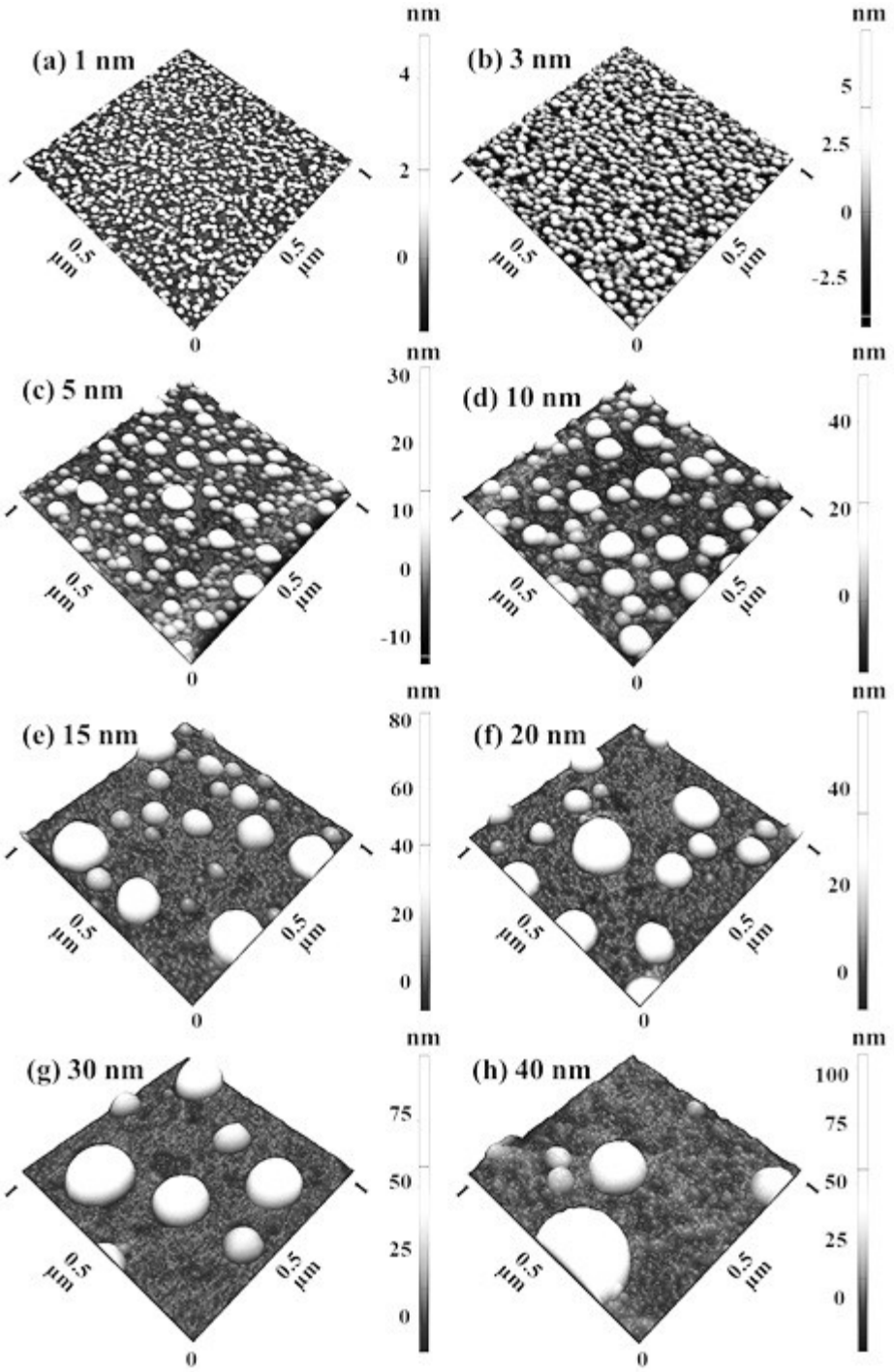

Figure S5: Small to large sized self-assembled Pd NPs on sapphire (0001) with 1 – 40 nm thick Pd films at 850 ^{o}C for 450 s. (a) – (h) 3-D AFM side-views of 1 × 1 µm^2. The corresponding scale bars represent the height with color variation.

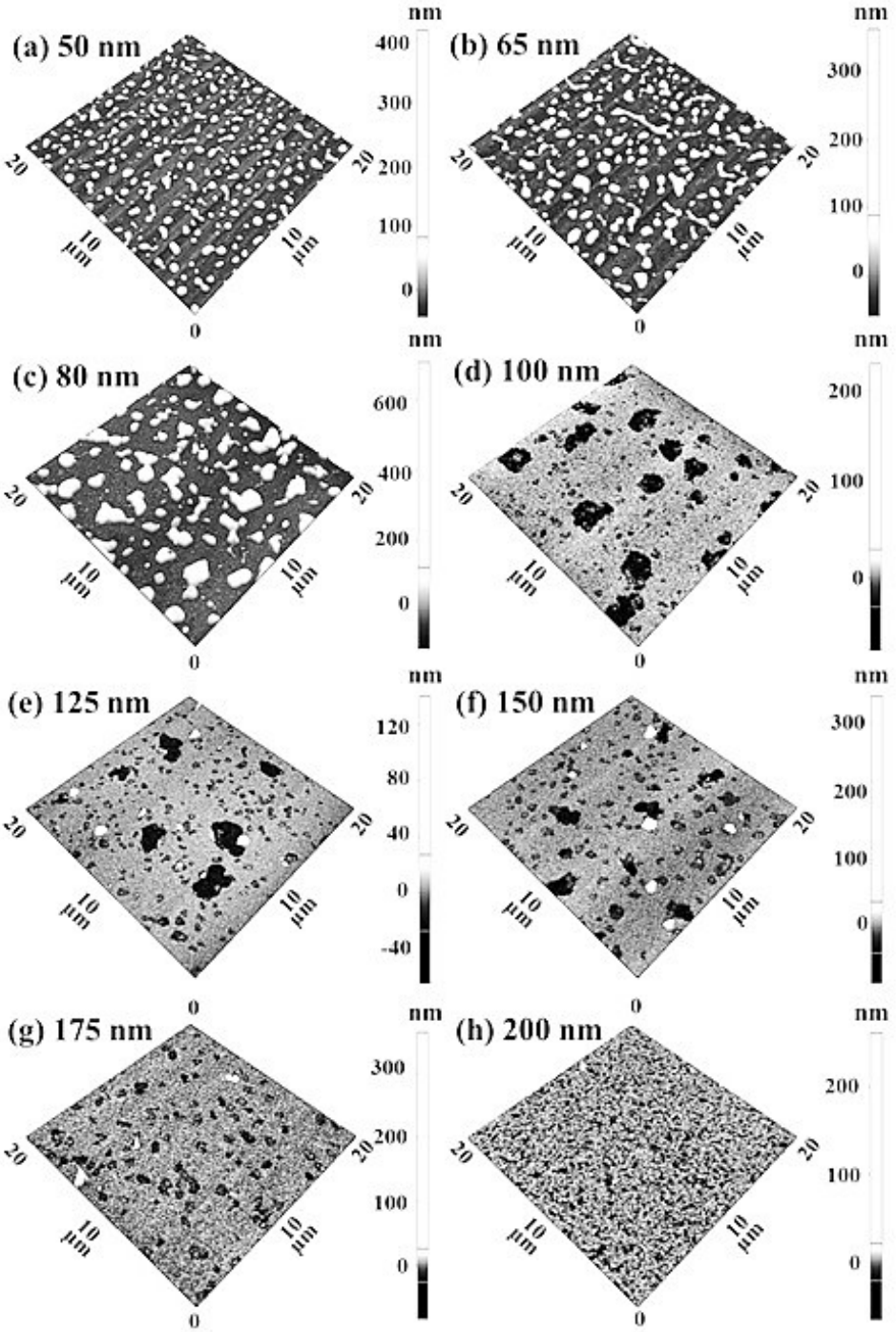

Figure S6: Effect of increased deposition amount between 50 to 200 nm on the evolution of Pd nanostructures and voids on sapphire (0001), annealed at 850 ºC for 450 s. (a) – (h) AFM side-views (20 × 20 μm^2).

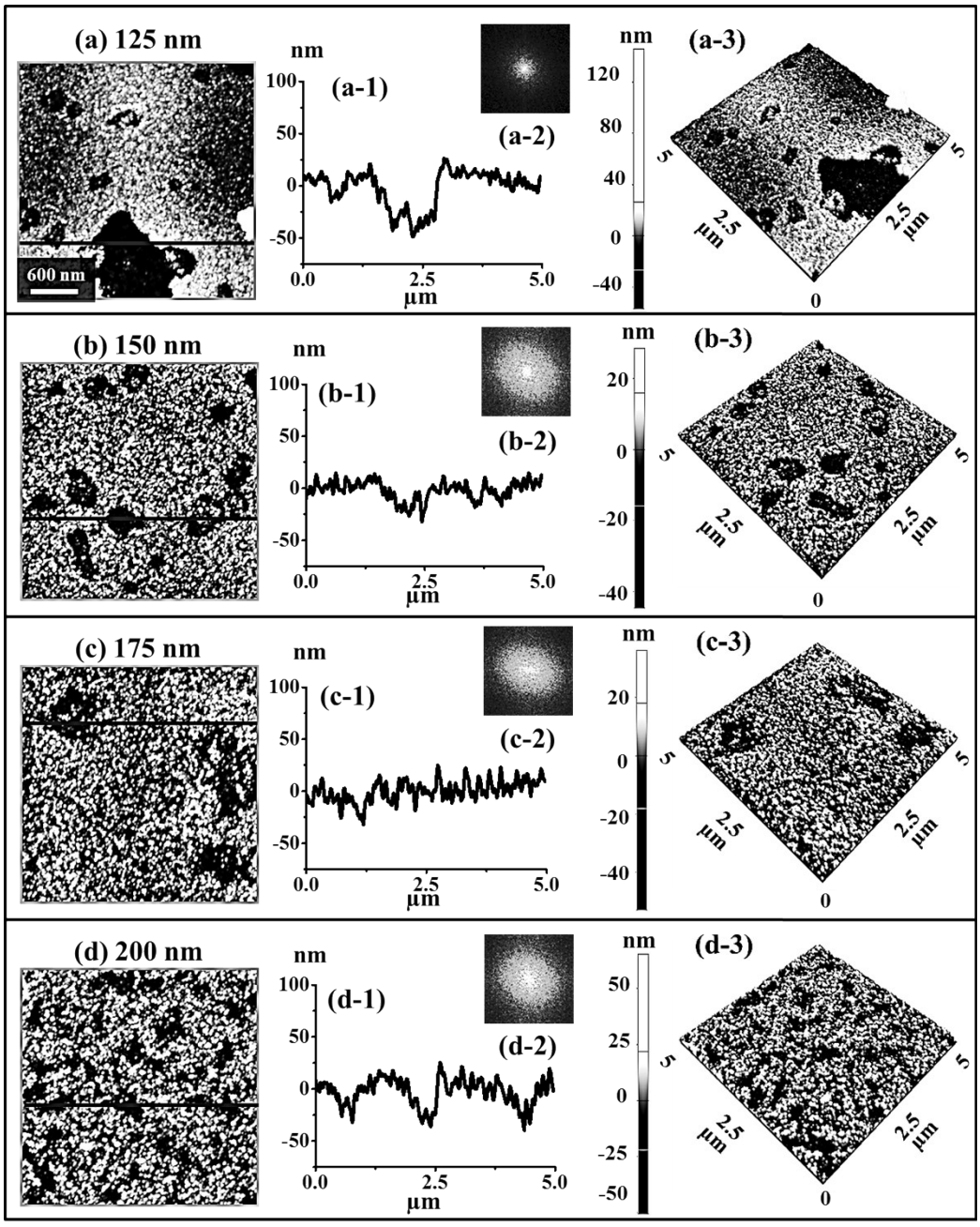

Figure S7: Formation of voids and their evolution with the deposition of Pd between 50 – 200 nm after annealing at 850 ^{o}C for 450 s. (a) – (d) AFM top-views of 5 × 5 µm^2. (a-1) – (d-1) Cross-sectional line profiles. (a-2) – (d-2) FFT power spectra. (a-3) – (d-3) Corresponding 3-D AFM side-views.

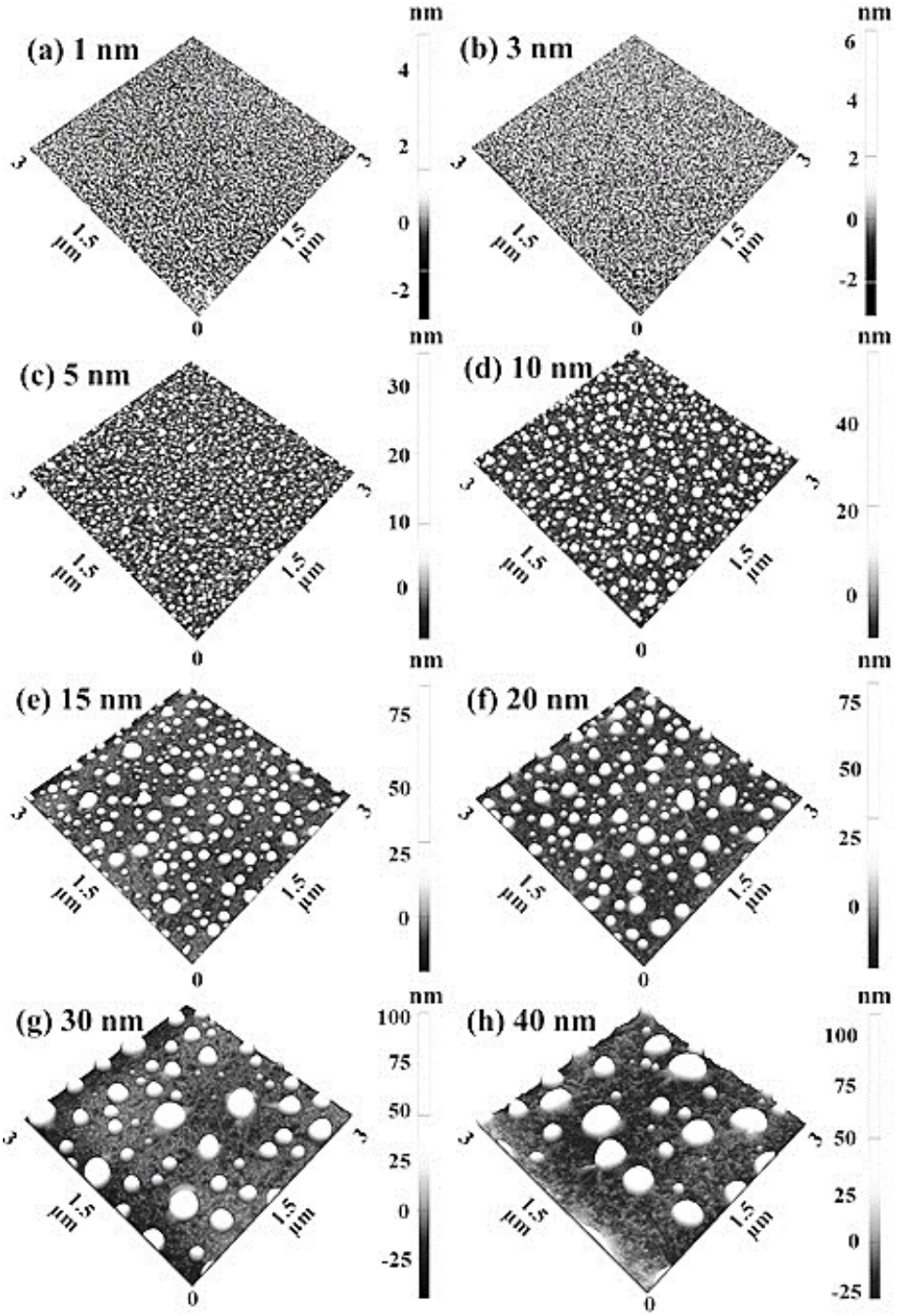

Figure S8: Morphological evolution of Pd NPs on sapphire at 800 ^{o}C for 450 s by the thickness variation of Pd between 1 and 40 nm. (a) – (h) AFM side views of 3 × 3 μm^2

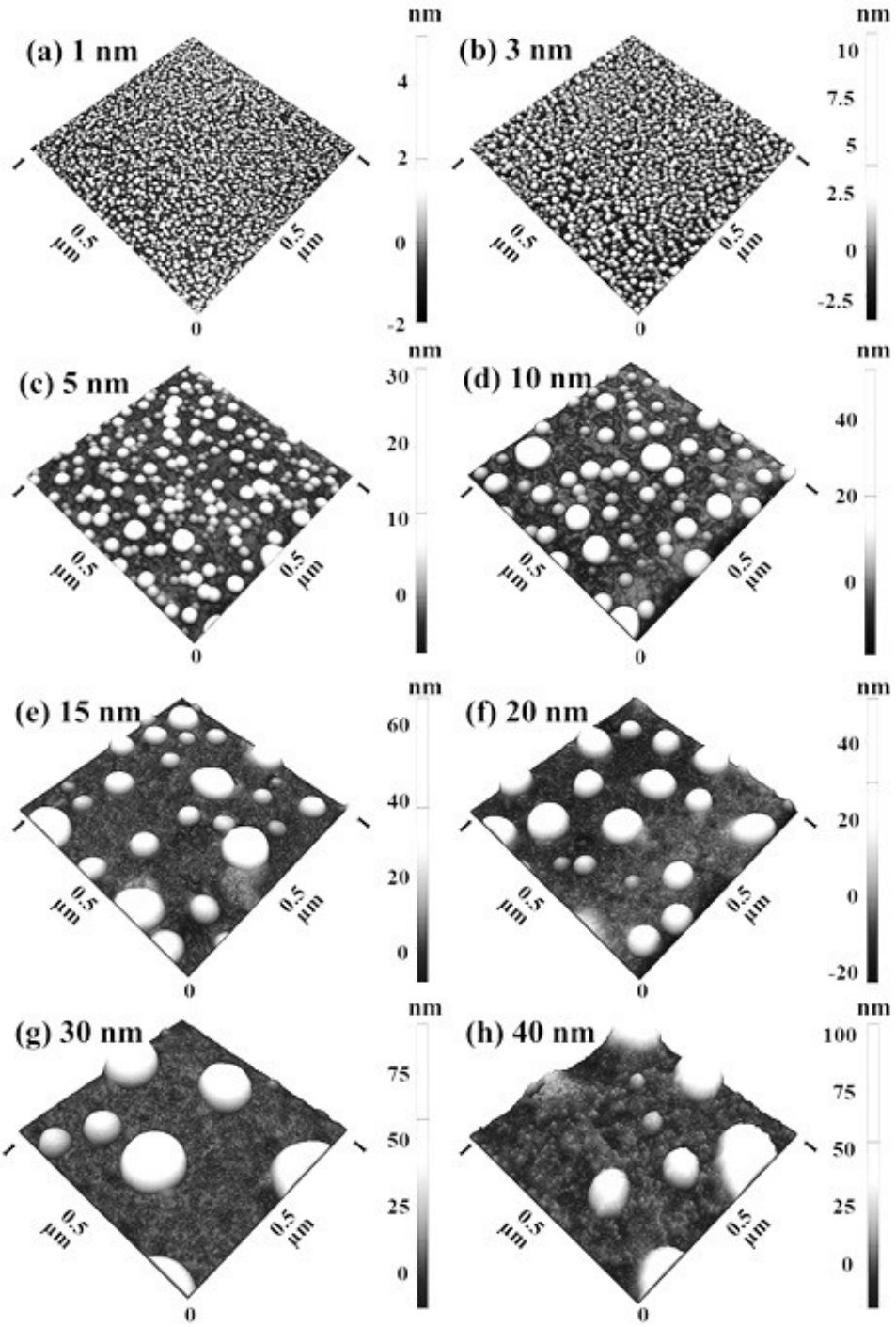

Figure S9: Enlarged 3-D AFM side views of 1 × 1 μm^2 showing the self-assembled Pd NPs at 800 ^{o}C for 450 s between 1 and 40 nm.

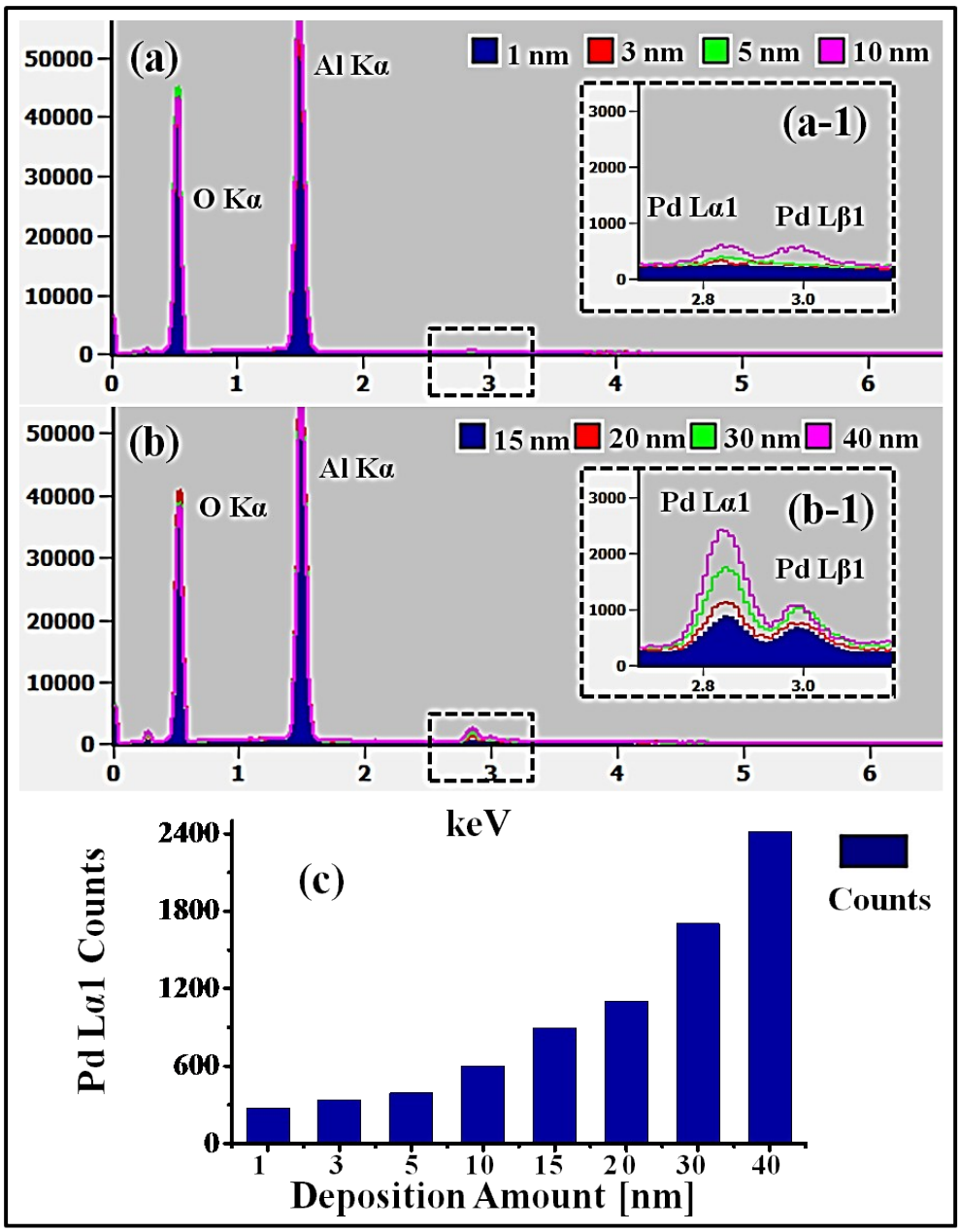

Figure S10: EDS spectra of the Pd nanostructures on sapphire (0001), annealed at 800 °C for 450 s with various thickness of Pd layers. Full range EDS spectra of samples with thickness (a) 1 - 10 nm and (b) 15 - 40 nm. (a-1) – (b-1) Enlarged spectra of selected region between 2.6 – 3.2 keV showing Pd Lα1 and Pd Lβ1. (c) EDS count plot as a function of deposition amount.

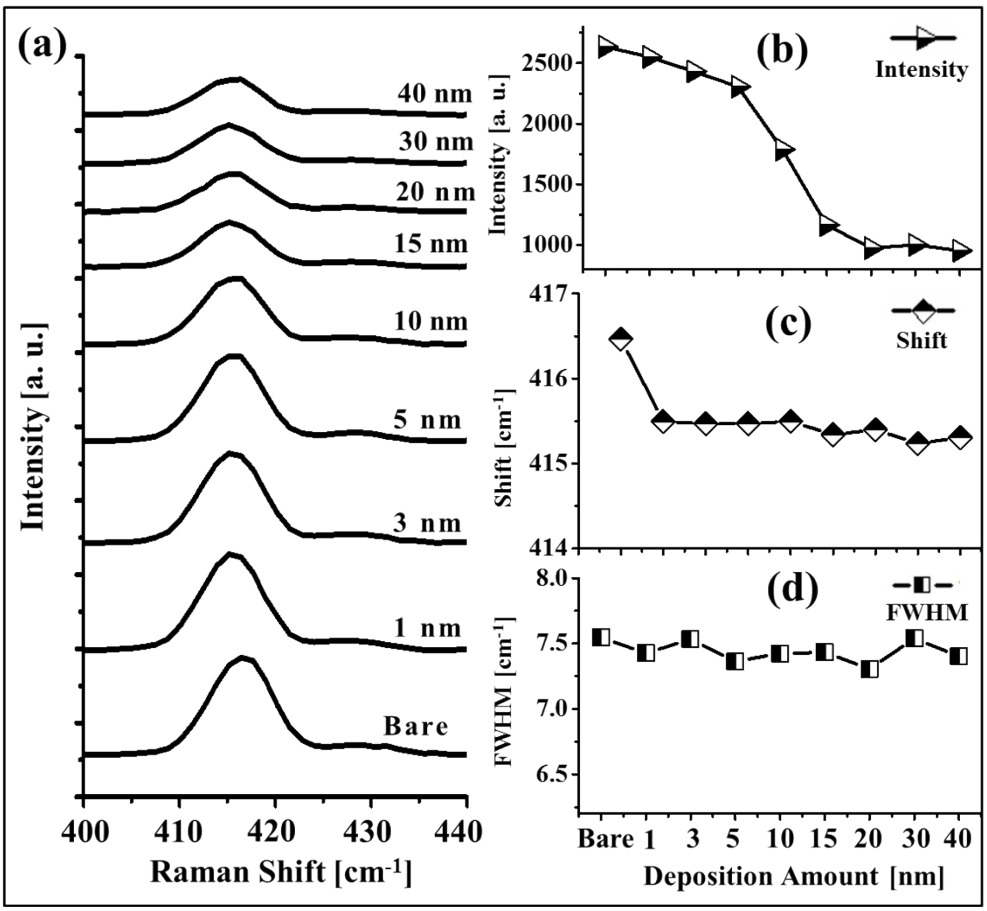

Figure S11: Raman spectra between 400 and 440 cm^{-1} showing the A_{1g} vibration modes for the samples with the Pd thickness from 1 to 40 nm annealed at 800 ^{o}C for 450 s.(b) – (d) Peak intensity, peak shift and full width at half maximum (FWHM) plots with respect to the deposition amount.

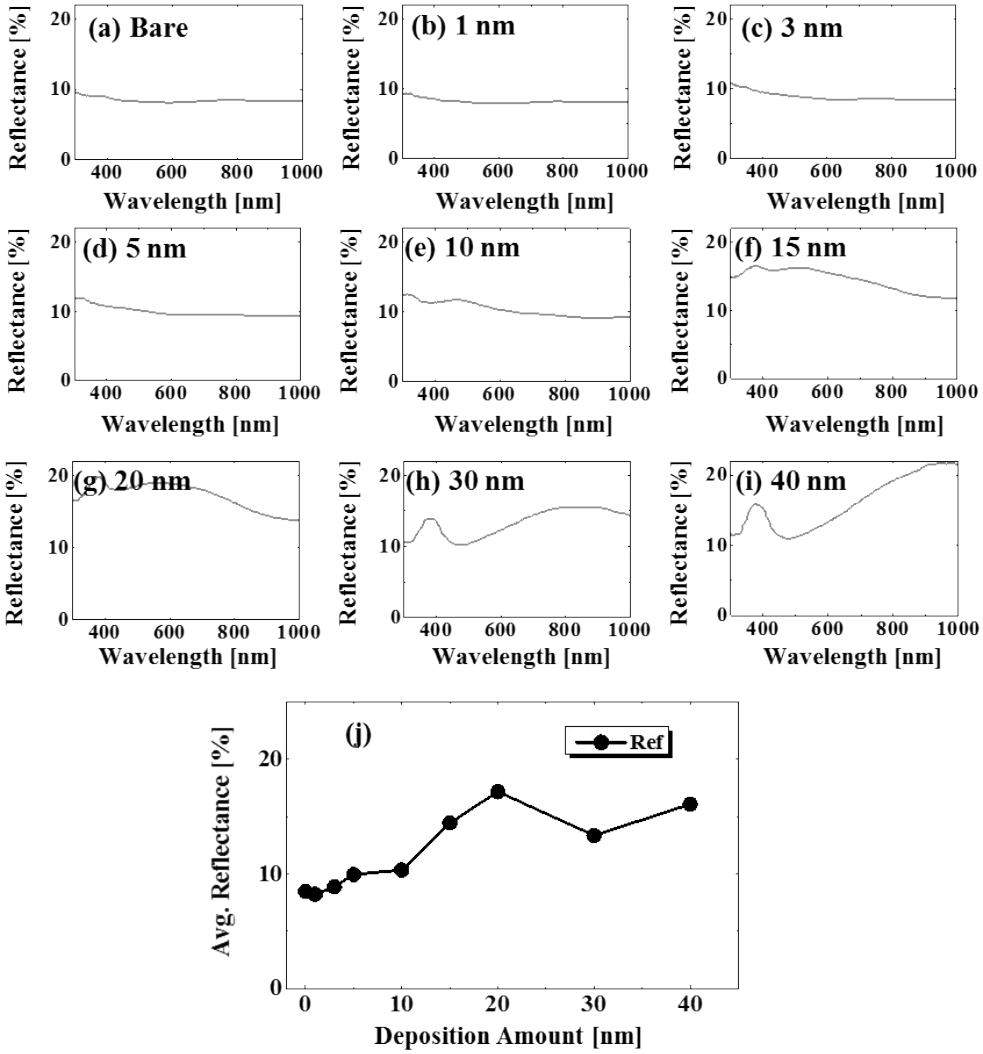

Figure S12: Reflectance spectra of Pd nanoparticles on sapphire (0001) fabricated with the deposition amount variation between 1 and 40 nm at 800 °C for 450 s: (a) bare sapphire, (b) – (i) samples with deposition amount as depicted. (j) Summary plot of average reflectance.

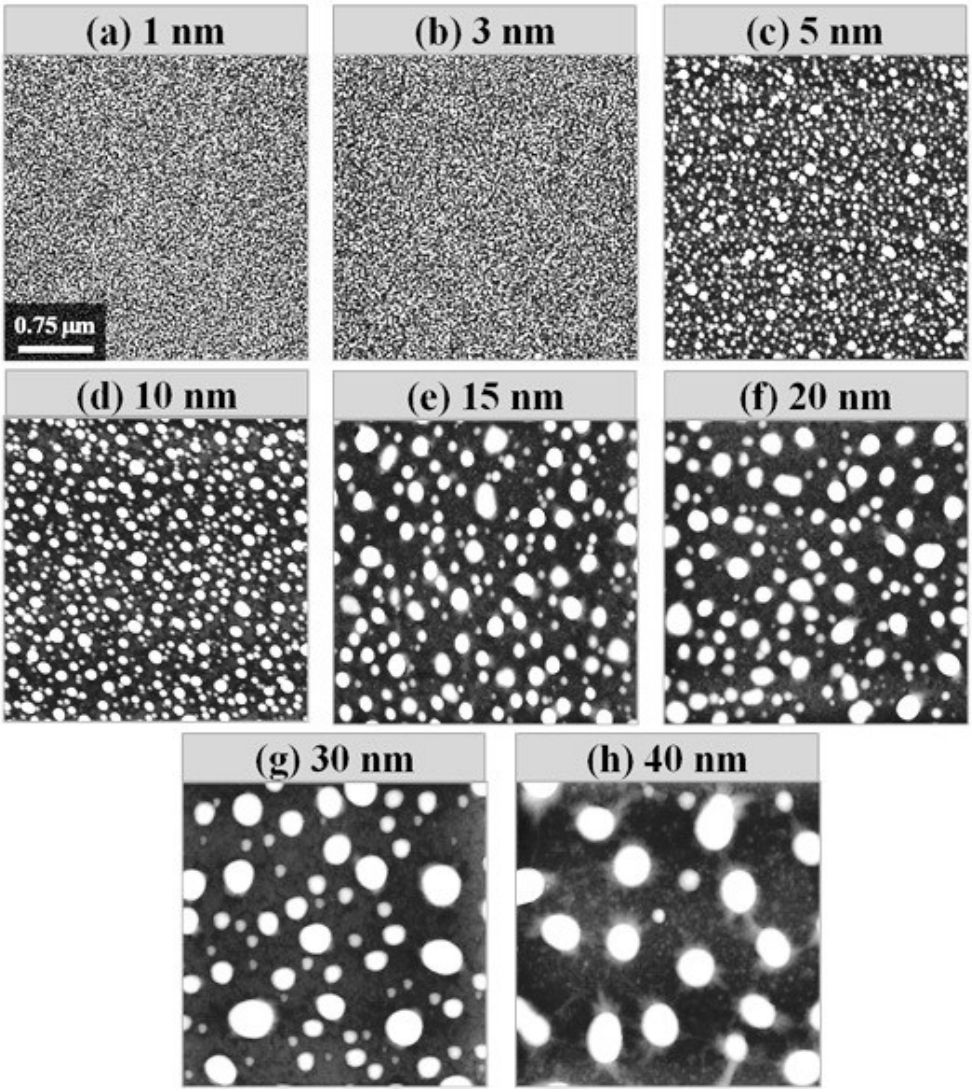

Figure S13: Formation of small to large sized self-assembled Pd NPs at 750 ^{o}C for 450 s along with the deposition amounts variation from 1 to 40 nm. (a) – (h) AFM top-views of 3 × 3 μm^2.

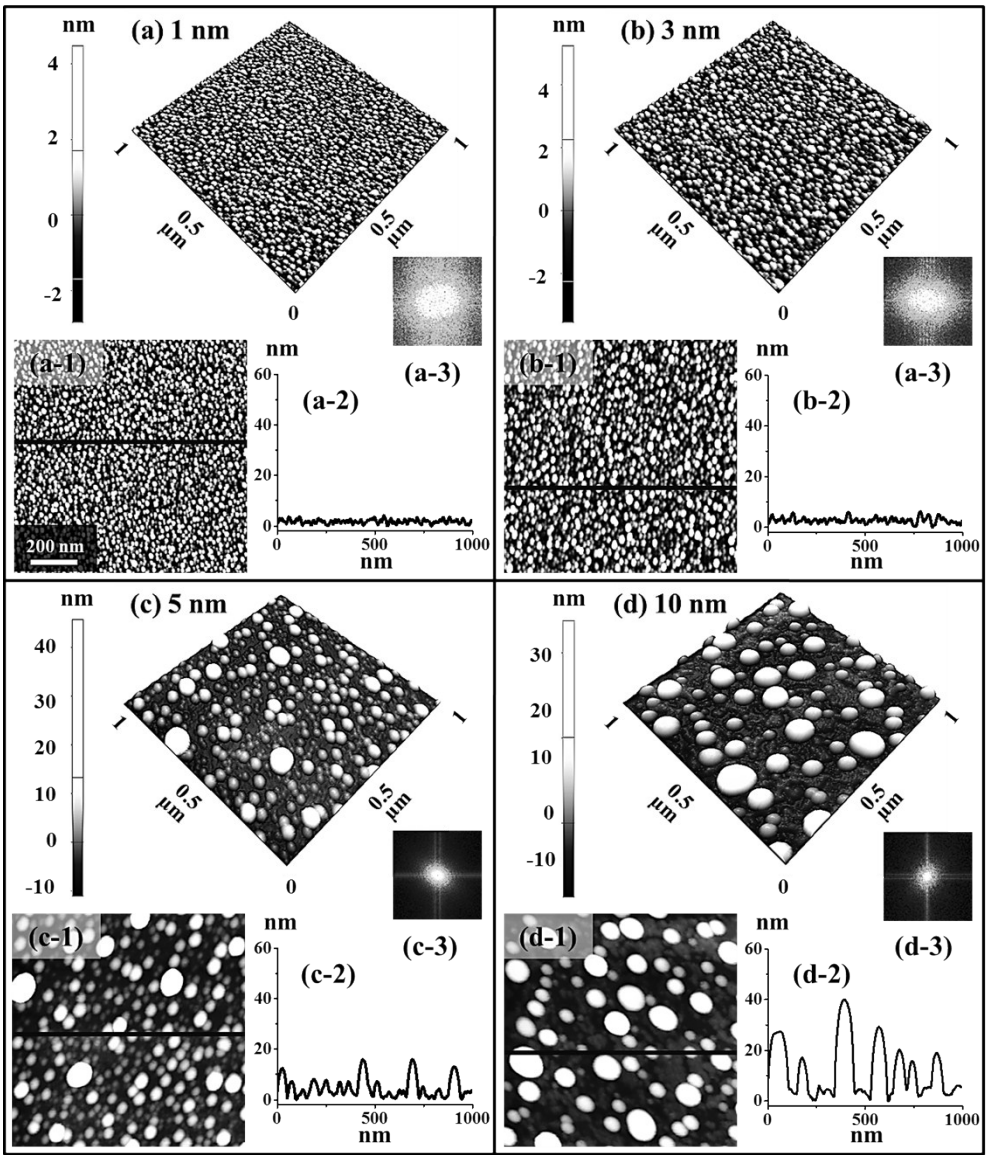

Figure S14: Evolution of small to medium sized self-assembled Pd NPs on sapphire, annealed at 750 ^{o}C for 450 s by the deposition amount variation between 1 and 10 nm. (a) – (d) AFM side-views of 1 × 1 μm^2. (a-1) – (d-1) Corresponding AFM top-views. (a-2) – (d-2) Cross-sectional line profiles. (a-3) – (d-3) 2-D - FFT power spectra.

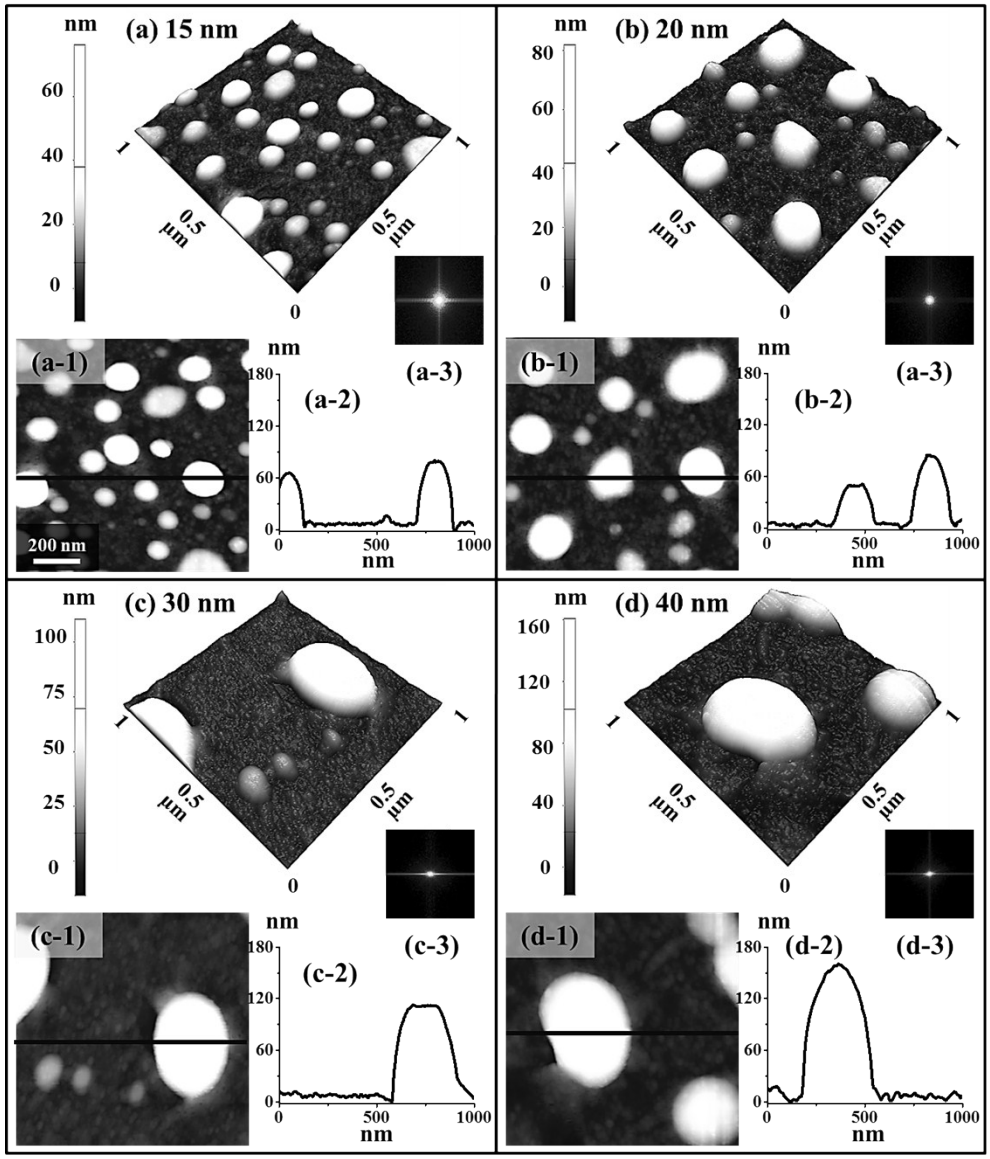

Figure S15: Formation of medium to large sized self-assembled Pd NPs on sapphire by the deposition variation between 15 and40 nm annealed at 750 ^{o}C for 450 s. (a) – (d) AFM side-views of 1 × 1 μm^2. (a-1) – (d-1) Corresponding AFM top-views. (a-2) – (d-2) Cross-sectional line profiles. (a-3) – (d-3) 2-D - FFT power spectra.

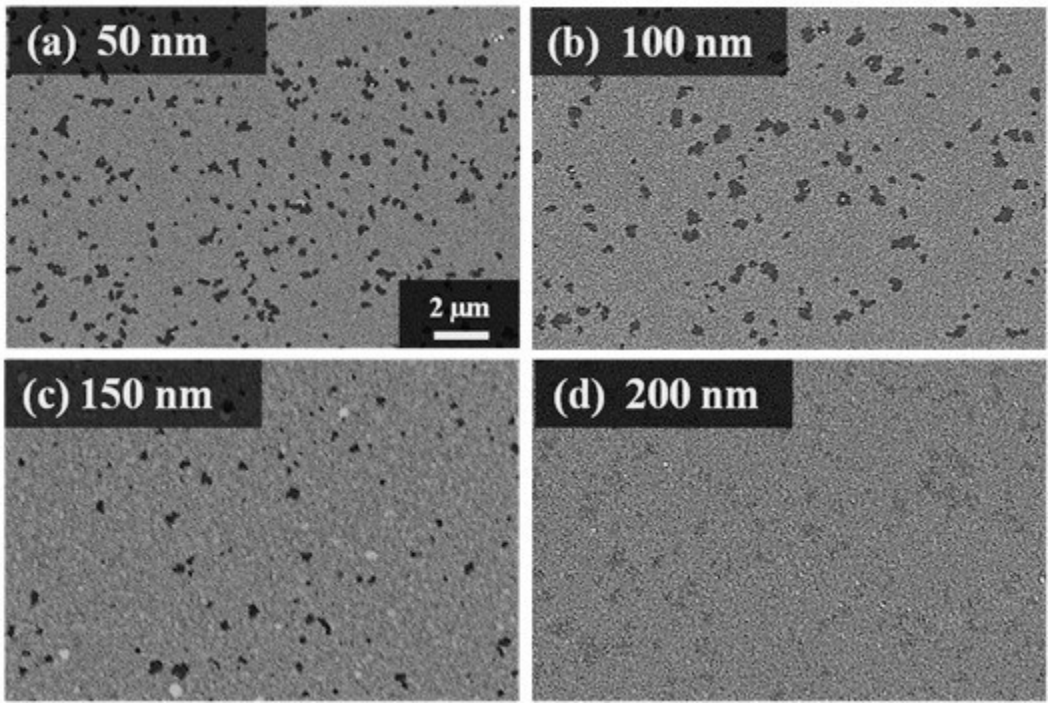

Figure S16: Scanning electron microscope (SEM) images of voids formed on Pd layers at 750 ^{o}C for 450 s with the deposition thickness from 50 to 200 nm.

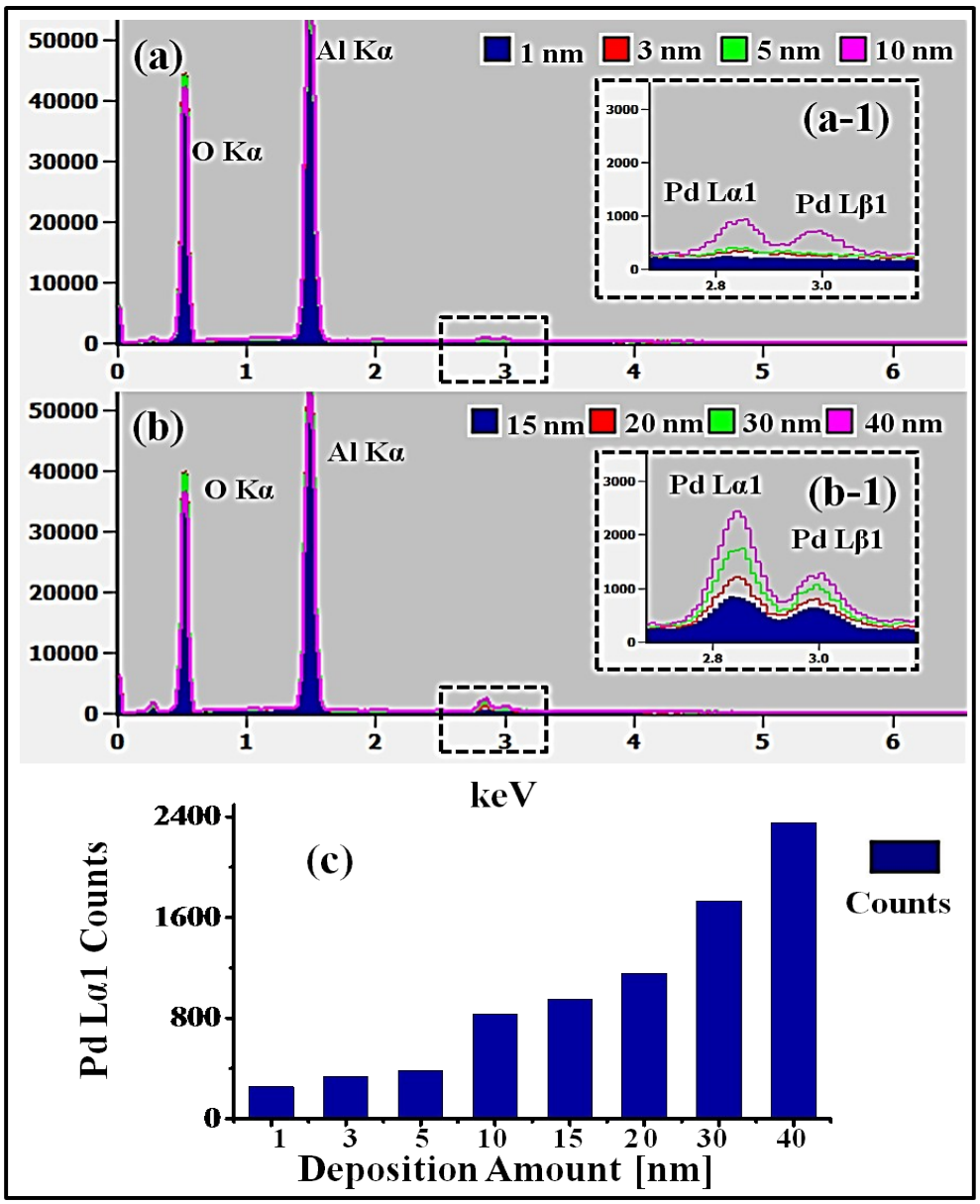

Figure S17: EDS spectra of Pd NPs on sapphire with the deposition amount variation between 1 and 40 nm and annealed at 750 °C for 450 s. (a) – (b) Full range spectra of the samples. (a-1) – (b-1) Enlarged view of the selected area. (c) Spectral counts of the Pd Lα1 as a function of deposition amount.

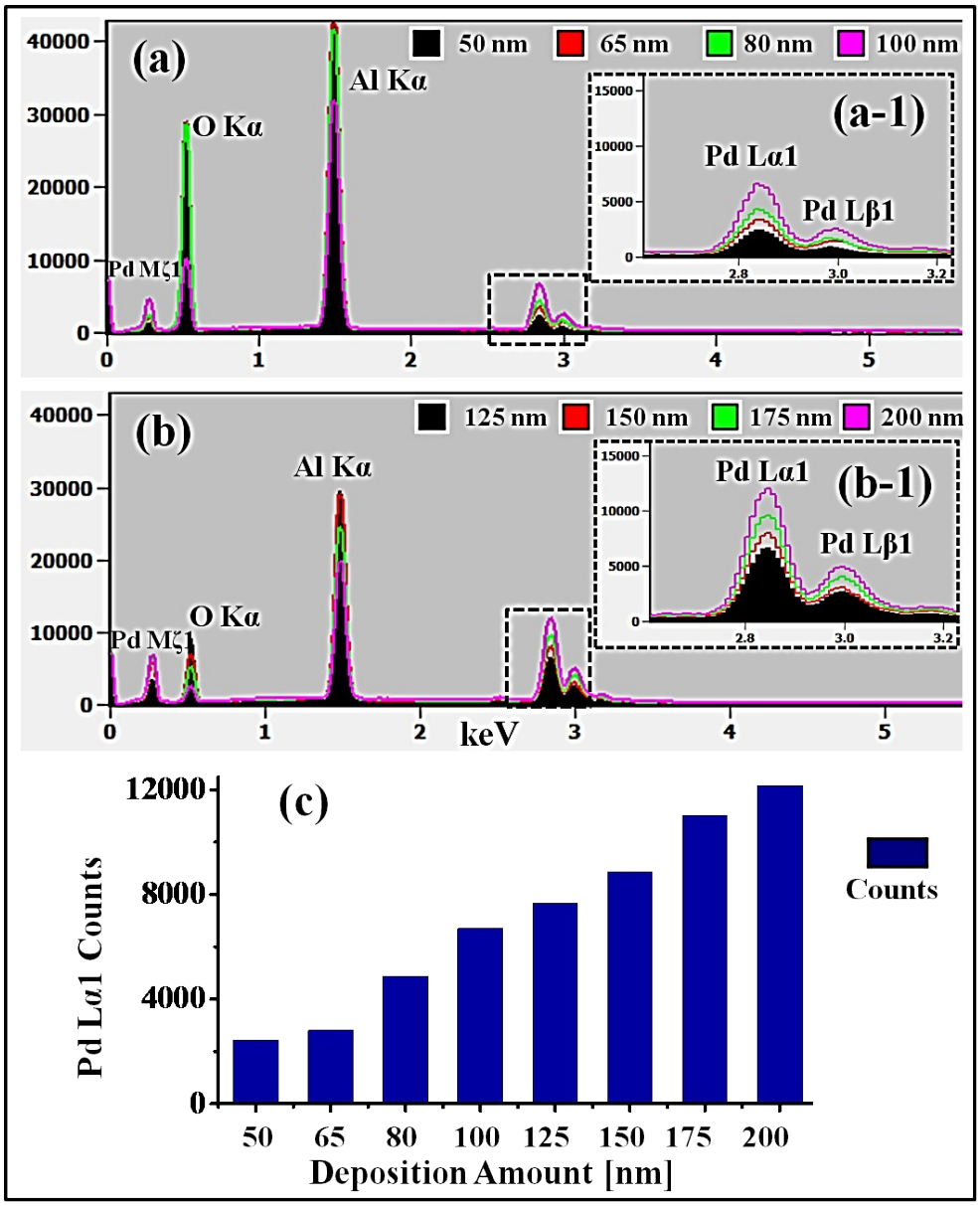

Figure S18: EDS spectra of samples with the deposition amount between 50 and 200 nm, annealed at 750 °C for 450 s. (a) – (b) Full range spectra of the samples. (a-1) – (b-1) Enlarged spectra. (c) Spectral counts of the Pd Lα1.

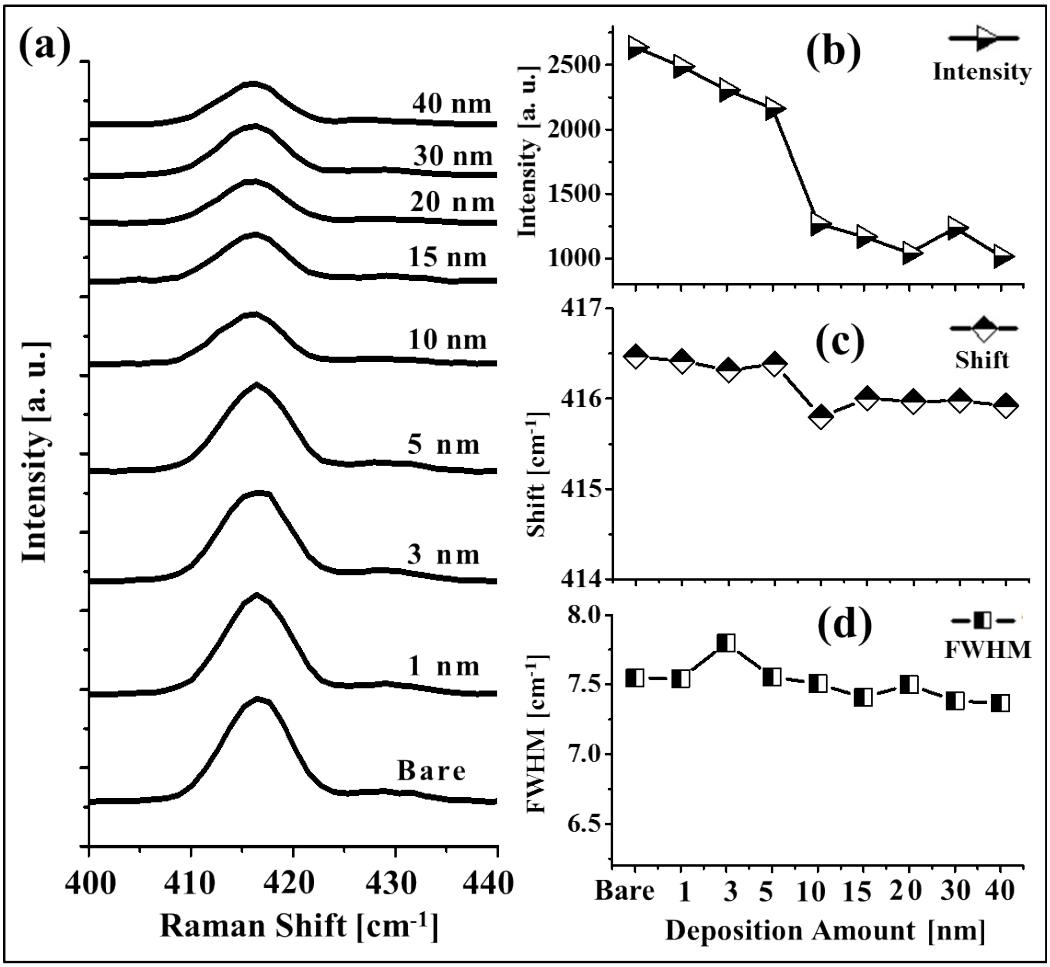

Figure S19: Raman spectra of Pd NPs at 750 ^{o}C for 450 s with the deposition amounts from 1 to 40 nm. (a) Spectral range of 400 to 440 cm^{-1}. (b) Plot of peak intensity, (c) peaks shift and (d) FWHM.

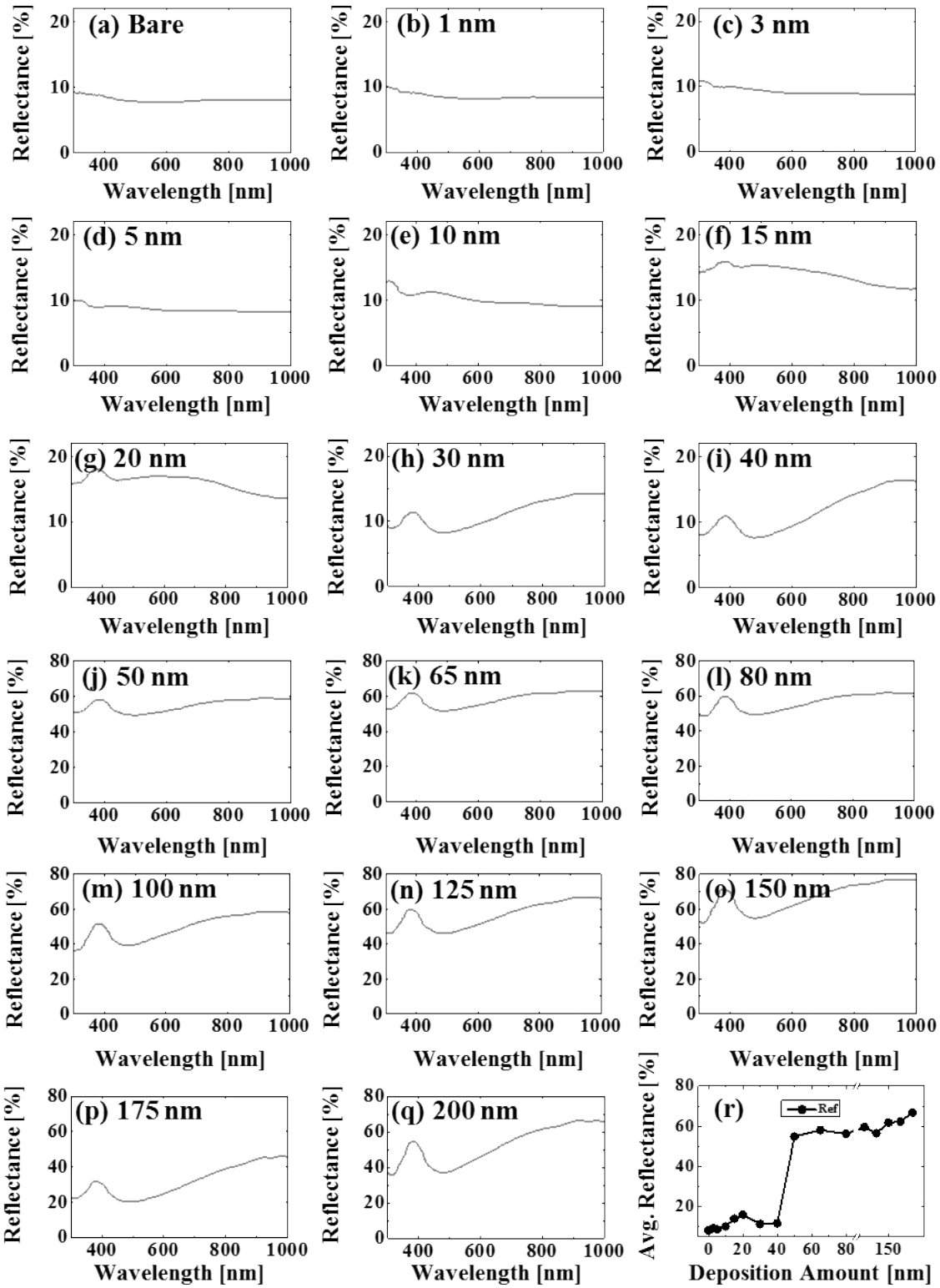

Figure S20: Reflectance spectra of the samples annealed at 750 °C for 450 s: (a) bare sapphire (0001), (b) – (q) from 1 to 200 nm Pd thickness. (r) Summary plots of average reflectance with respect to the deposition amount.

Table S1: Summary of RMS roughness (Rq) and surface area ratio (SAR) of Pd deposited samples before annealing after deposition with the deposition amount between 0.5 and200 nm.

Deposition Amount [nm]	Rq [nm]	SAR [%]
0.5	0.215	0.028
1	0.264	0.046
2	0.177	0.017
3	0.192	0.033
5	0.358	0.128
7	0.614	0.776
10	0.862	1.754
15	1.197	1.850
25	1.425	1.978
50	1.590	2.050
65	1.682	2.112
75	1.975	2.820
80	2.801	4.320
100	3.615	6.934
125	4.556	9.813
150	5.371	12.506
175	6.337	12.698
200	6.917	13.478

Table S2: Summary of Rq and SAR related to the Pd NPs fabricated on sapphire with the control of deposition amount at various annealing temperatures (fabrication at 750 - 850^{o}C for 450 s).

Deposition Amounts [nm]	Temperature					
	750 ^{o}C		800 ^{o}C		850 ^{o}C	
	SAR [%]	Rq [nm]	SAR [%]	Rq [nm]	SAR [%]	Rq [nm]
1	0.251	0.748	0.642	0.957	0.208	0.674
3	0.923	1.047	2.594	2.119	1.155	1.144
5	7.053	6.601	6.583	6.849	5.300	4.919
10	7.212	12.110	10.311	11.235	11.970	10.973
15	8.283	14.394	9.3080	14.698	10.405	15.169
20	8.223	16.081	9.030	17.24	9.714	16.875
30	7.205	28.605	8.187	24.798	9.168	24.753
40	9.496	34.641	10.046	30.181	10.541	26.054
50	1.087	3.121	-	-	8.565	45.731
65	1.044	2.745	-	-	9.337	56.782
80	1.683	3.118	-	-	6.117	47.635
100	2.850	6.301	-	-	3.384	13.49
125	2.003	3.945	-	-	4.029	18.48
150	4.156	7.055	-	-	4.877	8.115
175	4.108	5.689	-	-	5.540	9.266
200	5.258	9.341	-	-	6.829	11.228

Table S3: Summary of the average height (AH), average lateral diameter (LD) and average density (AD) of round dome-shaped Pd NPs on sapphire as a function of deposition amount of 1 – 40 nm (fabrication at 750 - 850°C for 450 s).

Deposition Amounts [nm]	750 °C			800 °C			850 °C		
	AH [nm]	LD [nm]	AD [$\times 10^8$/cm^2]	AH [nm]	LD [nm]	AD [$\times 10^8$ /cm^2]	AH [nm]	LD [nm]	AD [$\times 10^8$ /cm^2]
1	2.64	20.55	953	2.9	20.68	911	3.2	30.32	504
3	4.28	31.19	831	6.58	26.2	818	6.64	37.38	394
5	11.69	51.31	260	13.92	59.34	188	12.78	59.16	154
10	25.11	75.13	48	28.74	88.77	42	29.54	101.86	43.89
15	37.84	130.44	15.55	40.87	132.66	18.33	38.25	142.22	16
20	45.54	175.35	14	53.62	195.5	16.33	47.44	173.93	14
30	61.52	225.43	6.78	73.96	238.75	5.89	66.44	238.51	5.78
40	109.44	340.12	2.33	93.31	312.98	3.33	80.04	305.43	3.56

Table S4: Summary of Raman intensity (I), peak position (PP) and full width at half maximum (FWHM) of Pd nanostructures fabricated on sapphire (0001) with the control of deposition amounts from 1 to 80 nm at 750, 800 and 850 ^{o}C for 450 s.

Deposition Amounts [nm]	750 ^{o}C			800 ^{o}C			850 ^{o}C		
	I	PP [/cm]	FWHM [/cm]	I	PP [/cm]	FWHM [/cm]	I	PP [/cm]	FWHM [/cm]
Bare	2636.27	416.47	7.557	2636.27	416.47	7.557	2636.27	416.47	7.557
1	2550.63	415.49	7.426	2488.84	416.42	7.543	2513.16	415.25	7.325
3	2430.92	415.47	7.533	2305.76	416.32	7.796	2444.08	415.24	7.397
5	2304.91	415.47	7.363	2161.82	416.39	7.555	2187.32	415.34	7.425
10	1787.25	415.49	7.423	1268.70	415.80	7.506	1801.85	415.22	7.324
15	1164.26	415.34	7.432	1170.00	416.00	7.407	1264.94	415.14	7.399
20	974.28	415.39	7.305	1072.48	415.96	7.499	1051.17	415.04	7.584
30	1000.69	415.24	7.539	1236.95	415.97	7.383	1090.54	415.02	7.256
40	952.74	415.31	7.401	1017.35	415.92	7.366	1005.64	415.07	7.346
50	-	-	-	-	-	-	983.87	414.94	7.453
65	-	-	-	-	-	-	826.86	414.93	7.271
80	-	-	-	-	-	-	645.61	414.81	7.460

Table S5: Summary of the average reflectance for the samples with various Pd deposition amount from 1 to 200 nm after annealing at distinct temperatures: 750, 800 and 850 °C for 450 s.

Deposition Amounts [nm]	Reflectance [%]		
	750 °C	800 °C	850 °C
Bare	8.13	8.47	8.38
1	8.51	8.24	8.46
3	9.20	8.89	8.57
5	8.61	9.95	8.90
10	10.06	10.35	13.27
15	13.97	14.45	13.37
20	15.98	17.18	10.40
30	11.29	13.36	9.75
40	11.69	16.08	10.24
50	54.85	-	11.59
65	58.11	-	12.02
80	56.24	-	13.56
100	59.59	-	47.53
125	56.56	-	50.43
150	61.77	-	52.01
175	62.29	-	54.82
200	66.80	-	55.84