Electronic Supplementary Information (ESI) for

Morphological evolution of gold nanoparticles on silicon nanowires and their plasmonics

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Table S1. Detailed experimental parameters for the annealing of Si nanowire-Au nanoparticle heterostructures. Note: Sample #2, #6 are the baseline samples (bold and italics) and were repeated in each set (shaded).

Sample #	Duration (min)	Temperature (°C)	Atmosphere
1	15	625	Ar
2	***45***	***625***	***Ar***
3	75	625	Ar
4	120	625	Ar
5	45	300	Ar
6	45	500	Ar
2	***45***	***625***	***Ar***
7	45	700	Ar
8	45	800	Ar
9	45	1000	Ar
6	***45***	***500***	***Ar***
10	45	500	5%O_2/Ar
11	45	500	Vacuum
12	45	500	10%H_2/Ar
13	45	500	N_2

Table S2. Average size and inter-particle spacing of Au nanoparticles on the heterostructures before and after annealing at various conditions showing in Table S1.

Sample #	Conditions	Particle size (nm)	Inter-particle spacing (nm)
0	As-produced	10.40 ± 3.59	6.19 ± 2.30
Baseline conditions: temperature = 625 ˚C; duration: variable; in Ar environment.			
1	15 min	16.16 ± 12.88	10.09 ± 5.99
2	***45 min***	***18.72 ± 9.77***	***10.04 ± 4.14***
3	75 min	22.57 ± 17.09	12.20 ± 6.07
4	120 min	15.43 ± 7.48	11.65 ± 4.35
Baseline conditions: temperature: variable; duration = 45 min; in Ar environment.			
5	300 ˚C	16.82 ± 8.01	7.55 ± 5.86
6	500 ˚C	18.53 ± 12.67	9.60 ± 5.38
2	***625 ˚C***	***18.72 ± 9.77***	***10.04 ± 4.14***
7	700 ˚C	21.01 ± 14.50	10.34 ± 5.58
8	800 ˚C	23.81 ± 14.81	10.27 ± 5.98
9	1000 ˚C	114.04 ± 111.98	298.75 ± 186.66
Baseline conditions: temperature = 500 ˚C; duration = 45 min; environment: variable.			
6	***Ar***	***18.53 ± 12.67***	***9.60 ± 5.38***
10	5% O_2/Ar	16.26 ± 10.48	9.73 ± 5.09
11	Vacuum	16.23 ± 9.09	8.18 ± 4.86
12	10% H_2/Ar	20.20 ± 12.13	9.27 ± 4.74
13	N_2	18.31 ± 12.92	9.32 ± 5.27

Table S3. Binding energy of metallic gold and gold silicide ($AuSi_x$) derived from XPS analysis for Au $4f_{5/2}$ and Au $4f_{7/2}$ and the calculated molar fraction of metallic Au and shell thickness of gold silicide for the nanoparticles on the heterostructures before and after annealing.

Sample #	Conditions	Au $4f_{5/2}$		Au $4f_{7/2}$		$F_{Au, real}$ (%)	Shell thickness (nm)
		$AuSi_x$	Au	$AuSi_x$	Au		
0	As-produced	/	87.50	/	83.86	100	0
1	15 min	88.55	87.68	84.43	83.65	19.23	3.38
2	45 min	88.67	87.66	84.96	83.53	4.10	5.56
3	75 min	89.21	/	85.02	/	0	
4	120 min	88.78	/	85.04	/	0	
5	300 ˚C	88.46	/	84.68	83.55	3.43	3.04
6	500 ˚C	88.34	87.55	84.66	/	3.25	7.62
7	700 ˚C	88.51	/	84.81	/	0	
8	800 ˚C	88.70	/	85.00	/	0	
9	1000 ˚C	89.61	/	86.06	/	0	
10	5% O_2/Ar	88.37	/	84.68	83.70	6.52	4.56
11	10% H_2/Ar	88.26	/	84.47	/	0	
12	N_2	88.27	87.60	84.60	83.54	5.00	5.02
13	Vacuum	88.31	/	84.62	/	0	

Fig. S1 (A-C) HRTEM images of surface nanoparticles on the Si nanowire-Au nanoparticle heterostructures before (A) and after annealing for 15 min (B) and 45 min (C). (D-G) Measurement of lattice spacing for the Au nanoparticle corresponding to (A-C) using the DigitalMicro graph software.

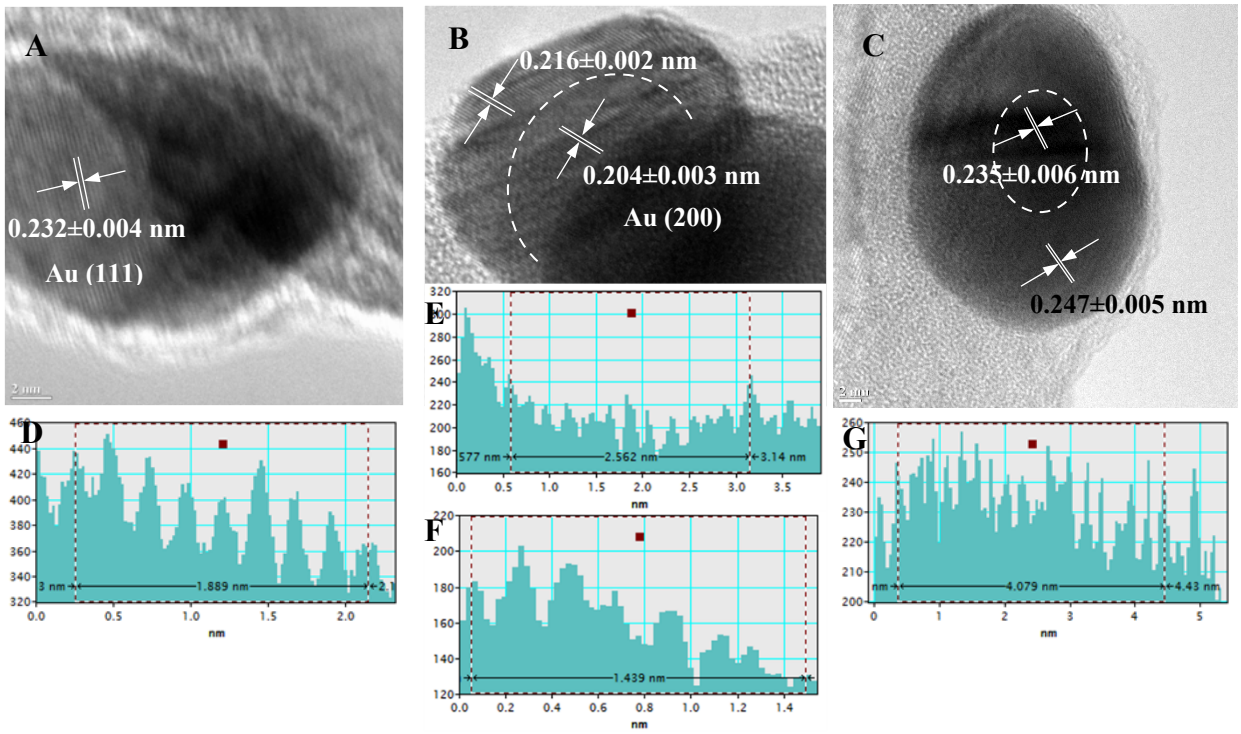
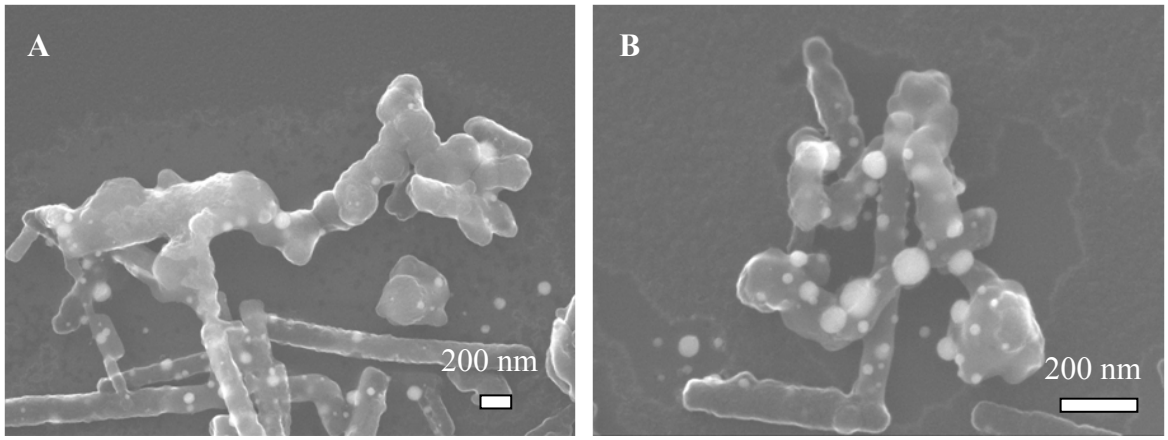


Fig. S2 (A, B) SEM images showing the Si nanowire-Au nanoparticle heterostructures after annealing at 1000 ˚C for 45 min in Ar environment. (C) Histogram showing the distribution of particle size and inter-particle spacing of nanoparticles on the heterostructures corresponding to (A) and (B).



C

Fig. S3 Histograms showing the distribution of particle diameter (A, C and E) and inter-particle spacing (B, D and F) of Au nanoparticles on the Si nanowire-Au nanoparticle heterostructures before and after annealing: (A, B) time set, (C, D) temperature set, (E, F) environment set.

A

B

C

D

E

F

Fig. S4 (A, B) STEM images of the Si nanowire-Au nanoparticle heterostructures before (A) and after annealing (500 ˚C, 45 min, Ar atmosphere). (C, D) EDS spectra obtained on the surface of Si nanowire (C, corresponding to (a) in (B)) and Au nanoparticle (D, corresponding to (b) in (B)). (E-F) EDS line profile corresponding to (A) and (B).

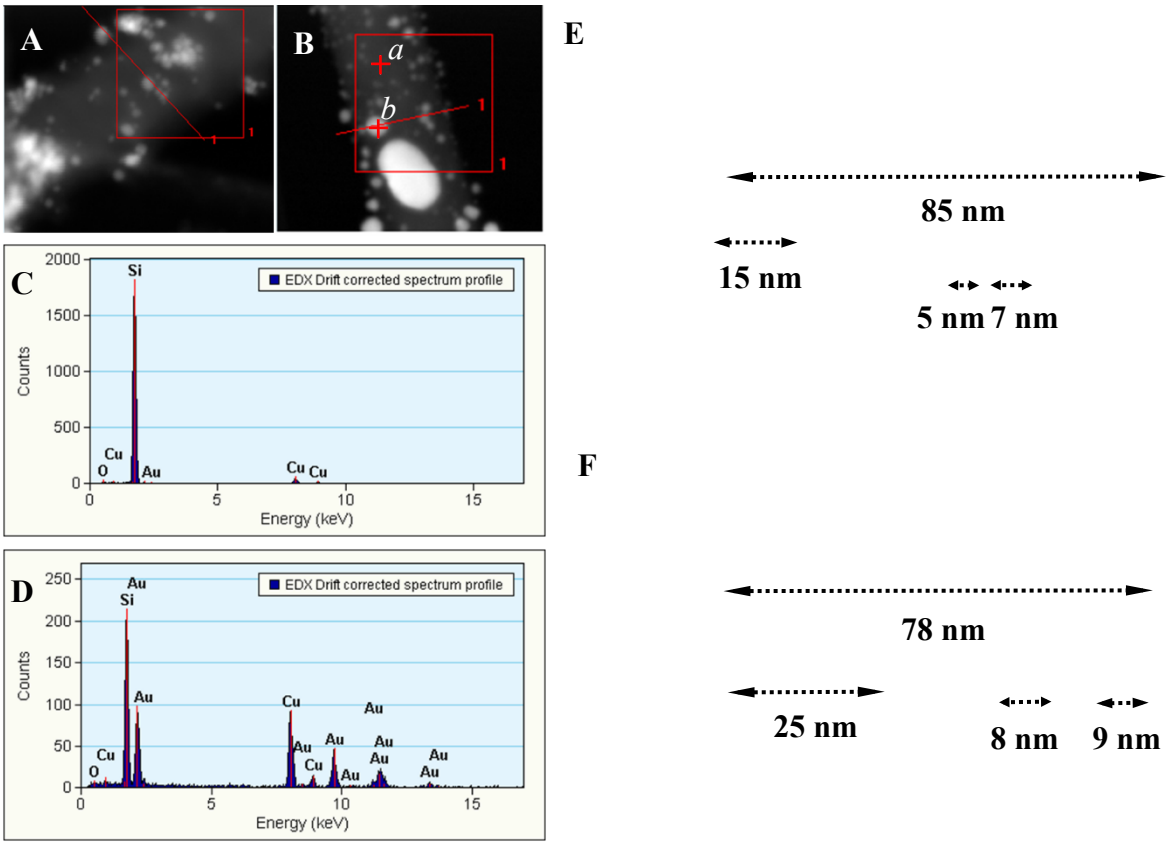


Fig. S5 (A) XPS spectra of the Si nanowire-Au nanoparticle heterostructures before and after annealing for various durations. (B-F) Deconvoluted XPS spectra (Au 4f) of the Si nanowire-Au nanoparticle heterostructures before (B) and after annealing for 15 min (C), 45 min (D), 75 min (E), and 120 min (F).

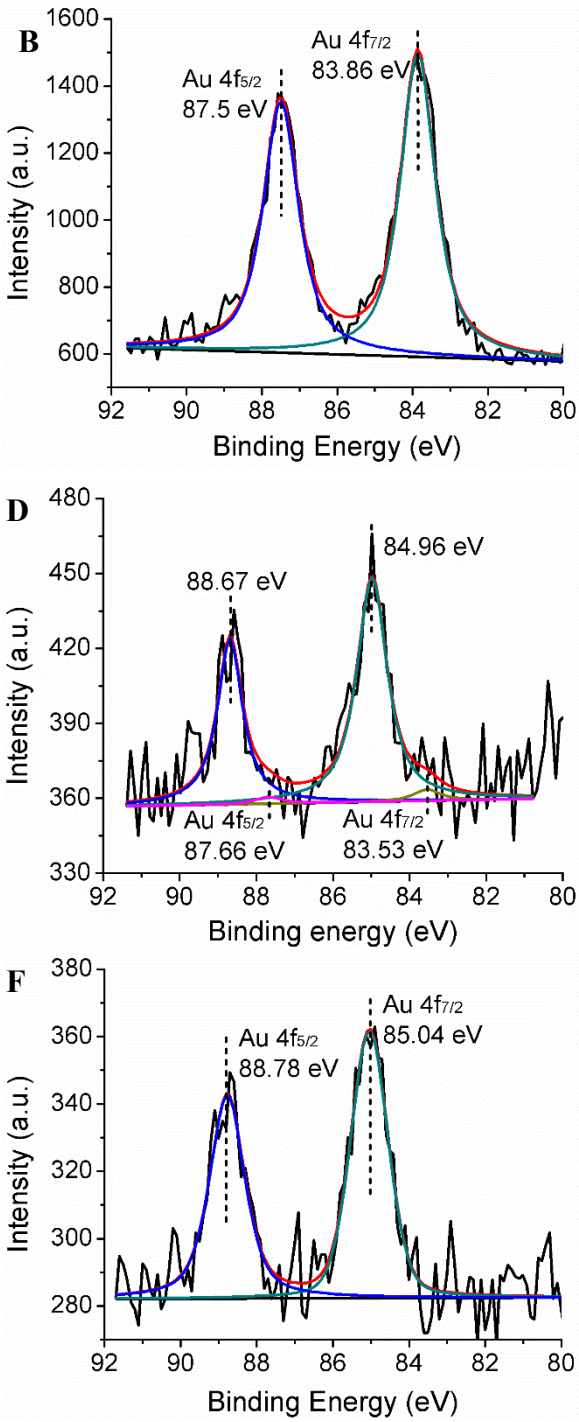


Fig. S6 (A) XPS spectra of the Si nanowire-Au nanoparticle heterostructures before and after annealing at various temperatures. (B-F) Deconvoluted XPS spectra (Au 4f) of the Si nanowire-Au nanoparticle heterostructures after annealing at 300 ˚C (B), 500 ˚C (C), 700 ˚C (D), 800 ˚C (E) and 1000 ˚C (F).

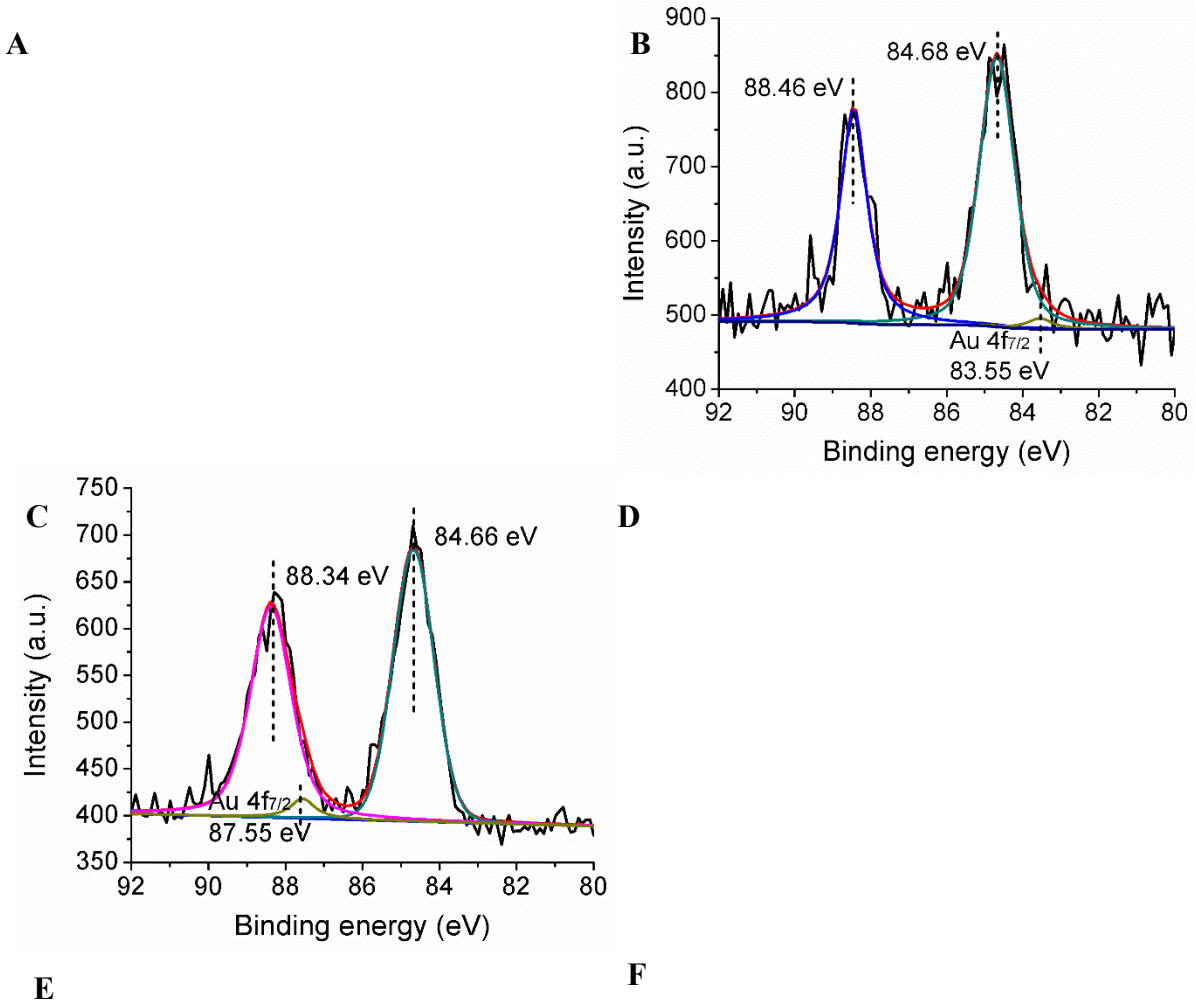
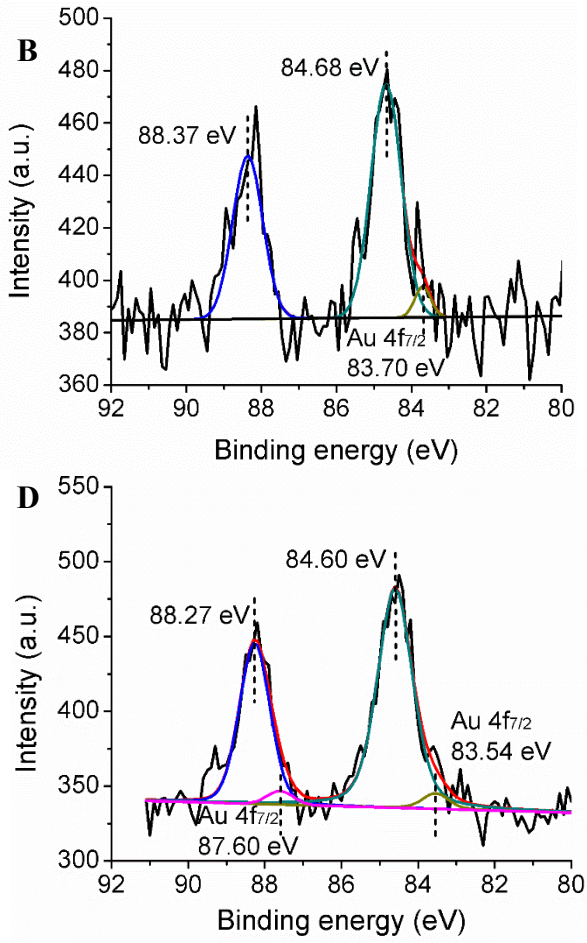


Fig. S7 (A) XPS spectra of the Si nanowire-Au nanoparticle heterostructures before and after annealing in various environments. (B-F) Deconvoluted XPS spectra (Au 4f) of the Si nanowire-Au nanoparticle heterostructures after annealing in (B) 5% O_2/Ar, (C) 10% H_2/Ar (D) N_2 and (E) Vacuum (~10 Torr).

A



C

E