Supporting Information

Fabrication of ultra-thin Silicon Nano-wire Arrays by Ion Beam-Assisted Chemical Etching

Zhiyuan Tan, Wenjia Shi, Chungang Guo, Quan Zhang, Liang Yang, Xiaolin Wu, Guoan Cheng and Ruiting Zheng*



Figure S1.Cross Section TEM image of a Si wafer, the wafer was pre-deposited 6 nm of Au layer and then implanted 5×10¹⁶ ions/cm² of Ag ions. The insert shows the HAADF-STEM (High-angle annular dark-field scanning transmission electron microscopy) image of the same sample. As shown in the TEM image, the alloy particles are three-dimensional distributed in the Si wafer. The larger ones are formed near the surface of the Si wafer which could directly contact with the etchant, and the smaller ones lies in the deeper area of the wafer which helps to cut the bigger gaps between larger particles into small gaps. The etchant can contact with the deeper catalysts in the wafer when the larger catalysts sinks into the wafer by the catalytic etching.



Figure S2. TEM image of Si nanowire arrays. Some separated Silicon nano-wires can be observed in the picture. The insert is the histogram of the diameters distribution

of SiNWs in the TEM, and the average diameter is 9.2 ± 2.5 nm.



Figure S3. Cross section SEM image of SiNWAs obtained with very low quantity of Ag. With the help of pre-deposited Au layer (3nm), SiNWAs can be achieved even the dose of implanted Ag ions is as low as 5×10^{15} ions/cm². The etching time is 80 min, and the etchant is HF/H₂O₂ mixed solution (30wt. %H₂O₂: 40wt. %HF: H₂O = 1: 12: 37 (vol %)).



Figure S4. HAADF-STEM image of the catalyst morphology obtained when the predeposited Au layer is 6 nm, and the implanted Ag ions is 5×10^{16} ions/cm². The three dimension distribution of the small particles(denoted as blue dash line) helps to cut the large caps between the big ones(denoted as red dash line) into small pieces(denoted as yellow dash line).



Figure S5.Influence of implanted Ag ion dose on the morphologies of SiNWAs. (a)-(c)The top view SEM images of the SiNWAs obtained by Ag ion implanting on the Si wafer with 6 nm of pre-deposited gold layer and further etching by the etchant, the implanted doses are 2.5×10^{16} ions/cm², 5×10^{16} ions/cm², 1×10^{17} ions/cm², respectively. (i)- (I) The cross-section SEM images of the SiNWAs obtained with implanted Ag ion dose of 2.5×10^{16} ions/cm², 5×10^{16} ions/cm², 1×10^{17} ions/cm², respectively. The insert shows a magnifying picture, the scale bar in the insert is 100nm. The etchant is HF/H₂O₂ mixed solution (30wt. %H₂O₂: 40wt. %HF: H₂O = 1: 12: 37 (vol %)) and the etching time is 40 min.

It's can be observed from Figure S5 a to Figure S5c, the top of the SiNWAs lean to each other when the Ag ion dose are 2.5×10^{16} ions/cm²(Figure S5 a) and 5×10^{16} ions/cm²(Figure S5 b), while the SiNWAs are almost free standing when the Ag ion

dose are 1×10¹⁷ ions/cm². The SiNWs made of 1×10¹⁷ ions/cm² Ag ion dose have much larger diameters(several hundred nanometers ,the insert of Figure S5f). And the diameters of the SiNWs made of 2.5×10¹⁶ ions/cm² Ag ion dose is about 20 nm (the insert of Figure S5d), which is larger than the SiNWs made of 5×10¹⁶ ions/cm² Ag ion dose (9.3 nm, the insert of Figure S5e). The reason may attribute to the catalysts morphology changes caused by the implanted Ag ion dose increases. The morphology of the SiNWAs gained by IBCE is close related to the morphology of the catalysts. When the implanted Ag ions is 2.5×10¹⁶ ions/cm², the quantity of Ag is insufficient to form the catalysts with gap less than 10 nm, that's why only the SiNWs with diameters about 20 nm are formed. With the Ag ion dose increase to 5×10¹⁶ ions/cm², small and high density alloy catalysts can achieved, and we can get the ultra-thin SiNWAs. When the dose of implanted Ag ions further increase, we find the diameter of SiNWAs reaches several hundred nanometers, just like the SiNWAs catalyzed by pure Ag films. This may due to the strong sputtering during ion implantation. According to the SRIM calculation, the sputtering of the Au atoms is 23.26 atoms/ion when the pre-deposited gold layer is 6 nm. So the more Ag ions implanted, the more Au atoms are sputtered away. When the implanted Ag ion dose is 1×10^{17} ions/cm², few Au atoms are left in the Si wafer. The main composition of the catalysts formed in Si wafer are Ag clusters with very little of Au. In such circumstance, the SiNWAs are similar with the SiNWAs produced with pure Ag as catalysts. We also observe the length of the SiNWAs is increasing with the increase of Ag ion dose, and the reason is similar with the result of changing pre-deposited Au layer.