

Motility of Metal Nanoparticles in Silicon and Induced Anisotropic Silicon Etching**

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Supporting information

Figure S1 SEM images of etched Si wafers pre-coated with Au nanostructures in aqueous HF-H₂O₂ solution. (a) Au nanostructure deposited on Si from aqueous HF-KAuCl₄ solution; (b) Top view of p-type 7-14 Ωcm Si(100) wafer etched in HF-H₂O₂ solution for 30 minutes at room temperature; (c) Cross-section view of p-type 7-14 Ωcm Si(100) wafer etched in HF-H₂O₂ solution for 30 minutes at room temperature; (d) Cross-section view of p-type 7-14 Ωcm Si(111) wafer etched in HF-H₂O₂ solution for 30 minutes at 50°C; (e, f) Cross-section and top views of p-type 4-7Ωcm Si(113) wafer etched in HF-H₂O₂ solution for 30 minutes, respectively.

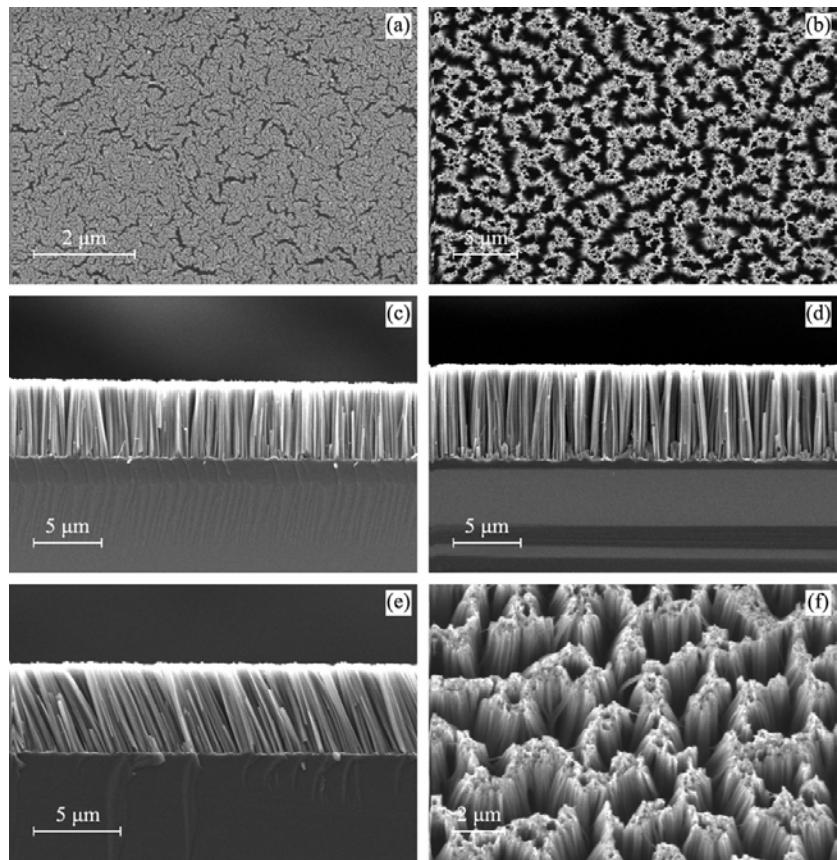


Figure S1

Figure S1 shows large-area aligned SiNWs could be similarly produced on Si surface coated with Au particles. Vertically aligned SiNW arrays could be produced on (100) and (111) Si wafers. Si(110) and Si(113) (Fig.S1e) wafers coated with Au particles yielded aligned SiNWs but slanted on Si surfaces. SEM cross-section view of the etched samples confirmed that Au particles located at the etching interface. The experiments show that Au particles could also lead to anisotropic etching of Si, and the most favorable moving direction of Au particles also is along the [100] orientation, which is the same as Ag particles.

Figure S2 SEM images of etched Si wafers pre-coated with Cu nanostructures in aqueous HF-H₂O₂ solution. (a) Cu nanostructure deposited on Si from aqueous HF-Cu(NO₃)₂ solution; (b) Top view of p-type 7-14 Ωcm Si(100) wafer etched in HF-H₂O₂ solution for 30 minutes.

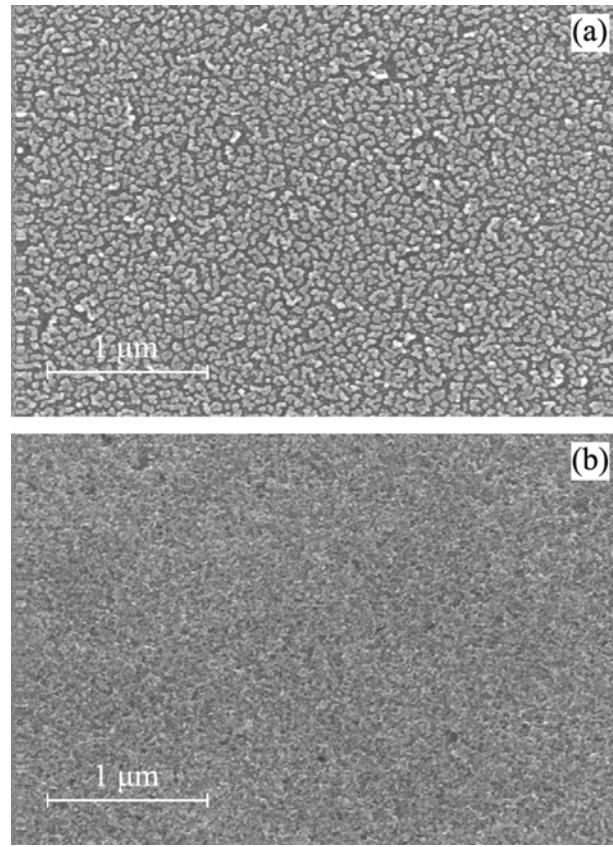
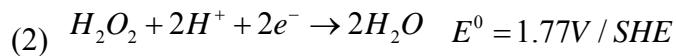
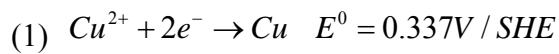


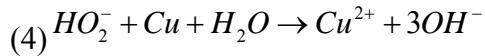
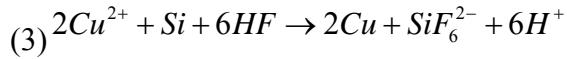
Figure S2

In contrast to Si wafers coated with Ag, Au, and Pt, Si surface coated with Cu nanostructures only showed shallow pits (Fig. S3b). This is caused by the dissolution effect of Cu particles during etching in HF-H₂O₂ solution. The dissolution rate of Cu depends on the pH and the redox potential of the etching solution. The dissolution reaction of Cu enhanced by H₂O₂ could be expressed by the following half-cell reactions:



Where E^0 is the standard redox potential vs. normal hydrogen electrode (SHE) as the reference electrode. While Cu²⁺ could extract electrons from Si and deposit on Si surface in

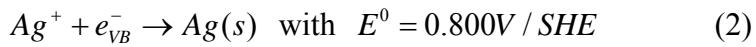
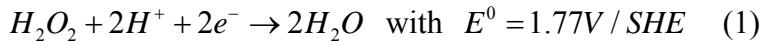
the form of metallic copper (3), the strong oxidizing ability of H₂O₂, especially the HO₂⁻, prevents Cu from re-deposition on Si surface (4).



Therefore, deep pits could not be created due to the quick dissolution reaction of Cu nanostructure on Si surface. In the cases of Au, Ag, and Pt nanostructures on Si surface, Au and Pt nanoparticles are passive to the etching of HF-H₂O₂; therefore, deep channels and SiNWs could be formed on Si due to their strong catalysis during etching.

2) Can silver particle dissolve and corresponding fluoride exist in HF-H₂O₂ solution?

In the presence of H₂O₂ in HF solution, dissolution of silver may be enhanced according to the following electrochemical reactions:



where E⁰ is the standard redox potential of the metal vs. standard hydrogen electrode (SHE) at 25°C. In this reaction, metal Ag is in a dissolved form, and the dissolution rate depends on the pH and the redox-potential of the solution (The redox-potential of the present solution is about 1.60 V). On the other hand, the Si surface is subjected to Si oxidation and etching by HF solution, then Ag⁺ ions take electrons from Si substrate and Ag deposition occurs through electron transfer process. The reaction can be described by the following reaction:



Thus, a competition between Ag dissolution and reprecipitation existed, which would finally reach equilibrium in aqueous HF-H₂O₂ solution. We assume that the competing

reactions are dependent on HF concentration and on the redox potential of solution. However, we did not observe any clear evidence of Ag dissolution, possibly due to very weak Ag dissolution, although dissolution could occur in the present HF-H₂O₂ solution. The weak Ag dissolution is supported by our SEM observations which confirmed that Ag particles directly sank into bulk Si with no evident change of morphological pattern due to dissolution. This can be clearly seen from Figure 7 in main text, which shows that the Ag film pattern collectively imprinted into bulk Si retaining its original Ag pattern.

In addition, we guess that the hydrate AgF·4H₂O or AgF ·2H₂O may exist in the solution; however, silver fluoride (AgF), unlike other silver halides such as silver chloride (AgCl), it is soluble in water to the extent of 1.8 kg/L due to the large solvability and ionization characteristics of F⁻ ion. Silver fluoride also is incompatible with strong oxidizing agents, strong acids. Therefore the silver fluoride is very unstable in aqueous HF-H₂O₂ solution. For the Ag particles present on silicon surface, the competitive between silver dissolution and its reprecipitation would finally reach equilibrium in aqueous HF-H₂O₂ solution. The stable silver particles present on the Si surface will produce local Si surface roughness increase and finally lead to formation of nanowires or nanoholes due to highly enhanced local chemical etching reactions.