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# Fluorinion transfer in silver-assisted chemical etching for silicon nanowires arrays

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ABSTRACT

Uniform silicon nanowires arrays (SiNWAs) were fabricated on unpolished rough silicon wafers through KOH pretreatment followed by silver-assisted chemical etching (SACE). Density functional theory (DFT) calculations were used to investigate the function of silver (Ag) at atomic scale in the etching process. Among three adsorption sites of Ag atom on Si(1 0 0) surface, Ag(T4) above the fourth-layer surface Si atoms could transfer fluorinion ($F^-$) to adjacent Si successfully due to its stronger electrostatic attraction force between Ag(T4) and $F^-$, smaller azimuth angle of F—Ag(T4)—Si, shorter bond length of F—Si compared with F—Ag. As $F^-$ was transferred to adjacent Si by Ag(T4) one by one, the Si got away from the wafer in the form of $SiF_4$ when it bonded with enough $F^-$ while Ag(T4) was still attached onto the Si wafer ready for next transfer. Cyclic voltammetry tests confirmed that Ag can improve the etching rate by transferring $F^-$ to Si.



## 1. Introduction

Silicon nanowires arrays (SiNWAs) have drawn much attention over the past two decades due to their potential applications in the fields of optics [1], nanoelectronics [2,3], renewable energy [4–9], lithium ion batteries [10–13], and biological and chemical sensors [14,15] as well. They can be fabricated by top–down or bottom–up approaches, such as vapor–liquid–solid (VLS) growth, electrochemical etching, and metal-assisted chemical etching. Among these methods, silver-assisted chemical etching (SACE) might be promising due to its high efficiency, low cost, simplicity, controllability and versatility.

For these reasons, recently a great deal of effort has been invested in preparing SiNWAs by SACE mainly based on $AgNO_3$ and HF. Peng K.Q. et al. reported a method to fabricate large-area SiNWAs in 2002 [16]. Hochbaum A.I. et al. developed a novel electroless etching synthesis of monolithic, single-crystalline, mesoporous SiNWAs with a high surface area and luminescent properties consistent with conventional porous silicon materials [17]. Yuan G. et al. investigated the morphology evolution of porous silicon nanostructures and thermoelectric characterization of SiNWAs of Electro-Less Etched (ELE) black silicon [18]. as treated as an atom with no charge the SACE mechanism in the perspective of primary battery at macroscopic scale while little attention has been focused on how $F^-$ was transferred to Si by Ag at atomic scale or by electrochemical analysis in the etching process. And almost all of their SiNWAs were formed on polished silicon wafers which are much more expensive than unpolished ones.

In this study, we fabricated uniform arrays of SiNWAs through SACE with a convenient way to pretreat unpolished rough silicon wafers beforehand. The mechanism of corrosion that Ag atoms transfer $F^-$ on Si (1 0 0) surface was further studied by density functional theory (DFT) calculations. Cyclic voltammetry (CV) tests based on three-electrode systems were applied to confirm $F^-$ transfer by Ag in the etching reaction.

## 2. Experimental

The single crystalline unpolished (1 0 0) silicon wafer (p-type, boron-doped, ~1 Ω cm, Xi Jing Electronic Corp., Xi'an of China) with a thickness of 200 ± 20 μm was cut into 1 cm × 4 cm rectangle samples along with cleavage plane. The samples were washed subsequently with ethanol and Piranha (a mixture solution of 3:1(v/v) $H_2SO_4$ (98 wt%)/$H_2O_2$ (30 wt%)) for 20 min. Then, they were put into 40 wt.% KOH aqueous solution at 90 °C with intermittent sonication for 2 min. After each cleaning step, the samples were rinsed with deionized water thoroughly. The cleaned samples were then immersed in 5 wt% HF solution for 2 min. The SACE to produce

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**Table 1**
Treatment of each Si sample.

| | Piranha | KOH | 5 M HF + 0.005 M $AgNO_3$ | 5 M HF |
|---|---|---|---|---|
| (a, b) Unpolished Si wafer | × | × | × | × |
| (c, d) SK10 min | √ | √ | × | × |
| (e, f) SA1 min | √ | √ | AT 1 min | × |
| (g, h) SE3 h | √ | × | AT 1 min | AT 3 h |
| (i, j) SKE9 h | √ | √ | AT 1 min | AT 9 h |

SiNWAs is based on a two-step process. In the first step, for a typical reaction, Ag nanoparticles (AgNPs) were deposited on samples by immersing in 50 ml aqueous solution of 5 M HF and 0.005 M silver nitrate ($AgNO_3$) for 1 min at ambient temperature (AT) and then they were sufficiently rinsed with deionized water to remove extra silver ions. The samples changed from metallic luster to colorfulness (light yellow typically), indicating a layer of AgNPs formed on the surface of samples. In the second step, the samples covered with AgNPs were immersed in a 50 mL etching solution containing 5 M HF for a given time (Table 1). Finally, the samples was copiously rinsed with deionized water and dried at room temperature.

Morphologies of etched samples were examined by scanning electron microscopy (SEM, Hitachi TM3000, FEI Quanta F250). CV tests were performed on a versatile multichannel electrochemical workstation (VMP2, Princeton Applied Research) with a voltage window from −0.3 to 1 V (vs. Ag/AgCl) and a scan rate of 200 mV/s. A piece of high purity platinum foil with large enough area was used as the counter electrode and a Ag/AgCl reference electrode with Polytetrafluoroethylene (PTFE) shell was applied to determine the potential of samples in etchant. The samples used for CV tests with AgNPs were immersed in 50 ml aqueous solution of 5 M HF and 0.005 M $AgNO_3$ for 1 min at ambient temperature.

## 3. Calculations

The surface Si(1 0 0) was modeled by periodically repeated slabs using superstructure (5 × 5). They contained five Si layers of atoms oriented along the [1 0 0] direction and a vacuum region of 15 Å was built on it. Dotted circles indicate the three possible on-top surface adsorption sites in the unreconstructed vertical plane, namely, bridge site (HB), valley bridge site (T3), and cave site (T4) [19,20], as shown in Fig. 1. The Ag was treated as an atom with no charge. The yellow atoms represent Si atoms in which the atoms on the top of the surface were emphasized in green.

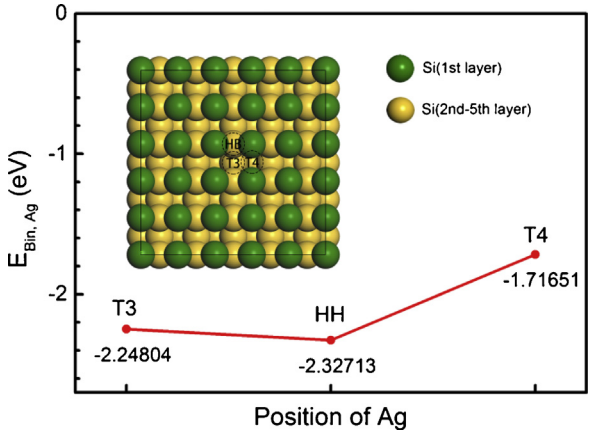


**Fig. 1.** Binding energy and top view (inset figure) of three absorption sites of Ag atoms on Si (1 0 0) surface. The dotted black circles represent Ag(T3), Ag(HB) and Ag(T4), respectively. The yellow atoms represent Si atoms of which the atoms on the top of the surface are emphasized in green.

Calculations were performed using CASTEP code, which adopts fully self-consistent DFT calculations to solve Kohn–Sham equations. The generalized gradient approximation (GGA), with the functional Revised Perdew–Burke–Ernzerhof (RPBE) [21,22] was employed. The electronic wave functions were expanded as a linear combination of plane waves, with a kinetic energy cutoff of 765 eV. The norm-conserving pseudopotentials for Si, Ag and F were used in all calculations. We used a method of Gaussian smearing to achieve self-consistent field convergence with a smearing value of 0.1 eV. The energy and force convergence tolerance was $2.0 \times 10^{-5}$ eV/atom and 0.05 eV/Å, respectively. All atoms were relaxed into their ground states by a conjugate-gradient algorithm except the bottom layer of silicon which was kept frozen mimicking bulk silicon.

## 4. Results and discussion

### 4.1. Characterization and morphology of SiNWAs

Fig. 2 confirms that SACE could fabricate uniform SiNWAs after KOH pretreatment. The rough surface of samples, as shown in Fig. 2(a and b), is probably the mechanical crystal faces damage layer generated in the mechanical wire-cut process, the average thickness of which is 25–30 μm according to industrial data. After KOH etching, the surface of Si(1 0 0) is much smoother than untreated one and clear ridges can make sure proper focus for SEM images (see Fig. 2 (c and d)). Ignoring the intermediate steps involved in the dissolution mechanism, the overall dissolution reaction for damage areas of Si(1 0 0) could be as follows [23]:

$$Si + 4H_2O + 2OH^- \rightarrow Si(OH)^{2-}{}_6 + 2H_2\uparrow \quad (1)$$

According to V. Lehmann, the preferential etching plane of Si wafer by KOH hot solution is Si(1 0 0) and the etching speed along Si(1 1 1) is the lowest (about two orders of magnitude lower than any other crystal plane). High $OH^-$ concentrations (e.g. > 40% for KOH) produce smooth surfaces while the etched surface becomes rough at low $OH^-$ concentrations. And the crystal faces damage layer on the surface caused by wire-cut process is prior to be etched than the inner unhurt layer, which is considered to be a self-limiting process and a superiority of alkali etching to acid etching [24]. Along with sonication, as a result, lattice damage areas and particles attached could be removed by KOH hot solution effectively. Fig. 2(e and f) shows that the sample surface was covered by a layer of AgNPs, after dipping into solution with 0.005 M $AgNO_3$ + 5 M HF for 1 min. Without KOH pretreatment ahead of SACE, as Fig. 2 (g, h) shows, $Ag^+$ may not be adsorbed homogeneously due to the existence of damage layers on the surface so that uniform SiNWAs could not be obtained. Fig. 2 (i and j) shows that samples were completely transformed into uniform SiNWAs after 9 h etching. The diameter of the SiNWAs was typically 50 nm approximately.

### 4.2. Calculations

#### 4.2.1. Binding energy of Ag at different position on Si (1 0 0)

In Fig. 1, $E_{bin,Ag}$ is the binding energy between the bulk and target Ag, and is calculated according to the formula:

$$E_{bin,Ag} = E_{Si-Ag} - \left(E_{Ag} + E_{Si}\right), \quad (2)$$

where $E_{Ag}$ is the energy of target Ag and $E_{Si}$ is the energy of Si(1 0 0) wafer. The value of $E_{bin,Ag}$ indicates the difficulty of the adsorption process. Larger differences (i.e. larger absolute value of $E_{bin,Ag}$, $|E_{bin,Ag}|$) reflect stronger adsorption.

Fig. 1 shows that the values of $E_{bin,Ag}$ of HB site is the highest when compared with other Ag sites, while that of T4 site is the lowest, indicating that Ag of HB site has the most tendency to be