Research progress of silicon nanostructures prepared by electrochemical etching based on galvanic cells

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Abstract—Metal-assisted etching of silicon in HF aqueous solution has attracted widespread attention due to its potential applications in electronics, photonics, renewable energy, and biotechnology. In this paper, the basic process and mechanism of metal assisted electrochemical etching of silicon in vapor or liquid atmosphere based on galvanic cells are reviewed. This paper focuses on the use of gas-phase oxidants O2 and H2O2 instead of liquid phase oxidants Fe(NO3)3 and H2O2 to catalyze the etching of silicon in the vapor atmosphere of HF aqueous solution. The mechanism of substrate enhanced metal-assisted chemical etching for the preparation of large-area silicon micro nanostructure arrays is summarized, and the impact of substrate type and surface area on reactive etching is discussed.

1. Introduction

Silicon nanostructures have important application prospects in solar cells, lithium batteries, thermoelectric conversion, biosensors, and other fields due to unique electrochemical properties, photoelectric properties, thermal conductivity, and other properties. Bai et al.[1] synthesized light-doped porous silicon nanowire arrays in one step based on HF/AgNO3/H2O2 etching system. They found that the surface morphology of these nanowires can be controlled by simple adjustment of H2O2 concentration. The concentration of H2O2 in the etching solution will affect the distribution of metal nanoparticles along the axis of the nanowire, which in turn affects the morphology of the silicon nanostructure. Yae et al.[2] used dissolved oxygen (O2) instead of H2O2 as the oxidant in the process of metal catalytic etching of silicon and studied the effect of HF concentration on etching rate and pore morphology. It was found that in the case of high HF concentrations, the etching rate has nothing to do with the HF concentration, and only depends on the catalytic activity of O2 and metal particles. In the case of low HF concentrations, the etching rate depends on the HF concentration and has nothing to do with the O2 concentration and the catalytic activity of metal particles.
This paper mainly introduces the basic process and mechanism of metal-assisted chemical etching in liquid and vapor phase to prepare silicon nanostructures based on the electrochemical reaction mechanism of galvanic cells, as well as the influence of graphite substrate on metal-assisted chemical etching, and discuss the influence of substrate types and surface area on the etching process.

2. Metal-Assisted Chemical Etching of Silicon Nanostructures

Metal-assisted chemical etching is one of the common methods to prepare silicon nanostructures in recent years because of its low cost, high efficiency, simple operation, and mild reaction conditions. Li and Bohn[3] first reported that a thin layer of noble metal was sputtered on the surface of the silicon substrate to catalyze the reaction of silicon in HF, H₂O₂, and M(NO₃)ₙ mixed solution to etch vertical porous or columnar one-dimensional silicon nanostructures. In 2002, Peng et al[4], adapted it for the fabrication of silicon nanostructures. Therefore, metal-assisted chemical etching technology has been widely used to prepare silicon nanoarrays of various specifications.

Metal-assisted chemical etching of silicon is an anisotropic wet etching, which can be generally divided into two stages: the first stage is to deposit a thin layer of noble metal (Au, Ag, Pt, Ni, etc[4-6]) nanoparticles on the clean silicon wafer, and the second stage is the formation of the silicon oxide layer and HF dissolution of oxide layer (common oxidants are H₂O₂, HNO₃ and M(NO₃)ₙ, etc[6]), and finally the silicon nanostructure is etched.

2.1. Mechanism of Metal-Assisted Etching of Silicon Nanostructures in Liquid Phase

Take the two-step etching of the HF/ H₂O₂/AgNO₃ system as an example, the preparation schematic diagram is shown in Fig.1a-c. When the clean silicon wafer is immersed in a certain volume ratio of HF/H₂O/AgNO₃ mixed solution, Ag⁺ captures electrons from the valence band of Si to form Ag atoms, which gradually gather on the surface of the silicon wafer to form silver nanoparticles. The silicon wafer plated with silver nanoparticles is immersed in the corrosive solution mixed with HF/ H₂O₂/H₂O with a certain volume ratio. As the electronegativity of Ag is greater than that of Si, the silver nanoparticles will capture electrons from the surface of Si to form a hole-rich area around it. At this time, H₂O₂ is reduced to water molecules on the surface of the silver nanoparticles, and the hole is consumed by Si to generate SiO₂, which is rapidly dissolved by HF. With the continuous oxidation and dissolution of Si, the remaining part forms silicon nanostructure[4].

![Fig.1 Schematic diagram of principle of metal-assisted chemical etching to prepare silicon nanostructures in liquid phase][5]
2.2. Metal-Assisted Etching of Silicon Nanostructures in the Vapor Phase

The common oxidants for the preparation of silicon nanostructures by metal-assisted etching in HF solution system are H2O2 and M(NO3)n and other substances, which are expensive and highly toxic. In the field of traditional metal materials, atmospheric corrosion is a common corrosion method. Oxygen is an environmentally friendly strong oxidant commonly existing in the earth's atmosphere. Due to the lack of a potential corrosion mechanism, the metal-assisted chemical etching process with oxygen as an oxidant has not been realized. Yae et al[7] studied the catalytic etching of silicon with O2 in the atmosphere instead of H2O2 as oxidant in the process of metal-assisted etching of nanostructures. The results show that O2 dissolved in HF solution can be used as an effective oxidant to promote the etching of Si and the formation of nano-porous silicon in the presence of noble metal particles, and the etching rate increases with the increase of oxygen content within a certain concentration range. Owen et al[8] exposed silicon coated with the metal catalyst to the vapor mixture of HF and H2O2, and explored the relationship between the average etching rate of Ag, Au and Pd/Au catalysts and the substrate temperature, and compared it with the traditional liquid-phase metal catalytic etching. The results show that compared with liquid-phase metal catalytic etching, low etchant concentration will significantly reduce the etching rate, which changes with the substrate temperature, and the metal catalytic etching in the vapor phase does not form microporous silicon as in the liquid phase, which can further improve the resolution and practicability of the metal catalytic etching process.

Hu et al[9] prepared silicon nanostructures and nanopore arrays by metal-assisted chemical etching of silicon in aerated HF/H2O vapor atmosphere and proposed the etching mechanism. They proved that metal-assisted chemical etching can be simply carried out in aerated HF/H2O vapor to prepare three-dimensional silicon nanostructures. In an aerated HF/H2O vapor atmosphere, the chemical etching of silicon can occur quickly because of the high oxygen content in the air, which can quickly pass through the thin liquid film to reach the silicon surface for reaction. As shown in Fig.2, the essence of metal-assisted etching of silicon nanostructures in HF/H2O vapor atmosphere is similar to that of etching in HF solution, which is based on the mechanism of galvanic cell electrochemical reaction. The reduction potential of O2/H2O in the aerated HF/H2O vapor atmosphere is higher than that of H+/H2, so oxygen molecules in the air can smoothly reduce and react with hydrogen ions in the electrolyte through the liquid membrane to generate water, and inject electron holes into the silicon wafer at the bottom of the metal particles, the holes are consumed by Si to become easily dissolved silicofluoric acid and hydrogen, and the remaining part forms silicon nanostructures. Metal-assisted chemical etching in gas-filled HF/H2O atmosphere to prepare silicon nanostructures is a simple, low-cost, and environmentally friendly method, it is different from the previous metal-assisted etching in solution, this method requires only plating the silicon wafer with the metal thin film is placed in the atmosphere of the hydrofluoric acid aqueous solution filled with air, and the etching reaction can occur. And it does not need strong oxidants such as nitrate hydrogen peroxide and can make full and efficient use of hydrofluoric acid, greatly reducing the amount of toxic reagent HF and the waste of water resources, which is conducive to the industrialization of silicon nanostructure preparation by this.

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\begin{align*}
\text{O}_2 + H^+ + H_2O &\rightarrow O_2H^+ + H_2O \\
\text{Si} + \text{HF} &\rightarrow \text{SiF}_6^{2-} + H_2
\end{align*}
\]

Fig.2 Diagram of silicon nanostructures prepared by metal-assisted etching in HF/H2O vapor [9]
3. Substrate-Enhanced Metal-Assisted Etching of Silicon Nanostructures

The essence of metal-assisted etching of silicon nanostructures in the gas/liquid phase is to promote the reaction by constructing local micro galvanic cells. Metal-assisted etching of silicon can prepare regular silicon nanostructures, but it is still a challenge to realize low-cost large-scale fabrication of silicon nanostructure arrays.

Liu et al. [10] studied that the connection of a silicon wafer coated with noble metal particles with a graphite electrode through a copper wire and placed it in an HF solution dissolved with O₂. The macro galvanic cell formed by the external loop promotes the preparation of silicon nanostructure by metal-assisted etching, and the silicon nanostructure array was successfully prepared. Chen et al. [11] studied the effect of the conductive back substrate of silicon wafers on the metal-assisted etching of silicon nanostructures by pasting insulating tape and different layer types of conductive carbon on the back of silicon wafers and etching them in HF/AgNO₃/ H₂O₂ solution for the same time. The results show that the length of the silicon nanowires array formed by the exposed silicon wafer and the silicon substrate with the insulating tape is almost the same, while the length of the nanowires array formed by adding different layers of conductive carbon on the back of silicon wafers is significantly increased, and the sidewall of the nanowires are smoother. It shows that the conductive back substrate can significantly increase the metal-assisted etching rate and prevent the generation of nanopores in the etching reaction.

Hu et al. [12] used that silver-plated P-type (100) and N-type (100) silicon wafers to directly contact a conductive graphite plate, and then etched them together in HF solution dissolved with O₂ to prepare silicon nanostructures. The results show that the silicon micro/nanostructure arrays are generated on the surface of the two types of silicon wafers, and the arrays are perpendicular to the surface of the silicon substrate. The sidewalls of the silicon wires are smooth without any impurities.

3.1. The Mechanism of Substrate Enhanced Metal-Assisted Etching

Substrate enhanced metal-assists etching of silicon nanostructure arrays in an HF solution with dissolved oxygen, which is a synergistic effect of metal nanoparticles and the substrate. Due to the electrode potential difference, the silicon and the noble metal nanoparticles on the surface form a local micro galvanic cell. The substrate and the silicon wafer are in direct contact and placed in a hydrofluoric acid solution to form a macroscopic galvanic cell [12], which jointly promotes the occurrence of the etching reaction. O₂ dissolved in the hydrofluoric acid solution undergoes a reduction reaction on the surface of the noble metal particles and graphite, and is reduced to water molecules. Electron holes are injected into the silicon wafer, the silicon obtains holes and is oxidized, and the formed oxide is corroded by hydrofluoric acid to form highly soluble hydrofluoric acid.

3.2. Influencing Factors of Substrate-Enhanced Metal-Assisted Etching

The size and type of the substrate surface area will greatly affect the morphology of the silicon nanostructures produced by metal-assisted etching [10-12]. Liu et al. [10] etched silicon nanostructures under the condition that the area ratio of the P-Si(100) wafer and the graphite substrate were 1:20 and 1:8 in the HF solution dissolved with O₂, and found that with the increase of graphite plate surface area, the silicon nanowire array obtained from the silicon surface is longer. The increase in the surface area of the graphite plate can increase the rate of graphite plate-enhanced metal-assisted etching of silicon, the electronegativity of the graphite plate is greater than that of silicon, and the ability to obtain electrons is stronger. In the reaction process, the graphite plate acts as the cathode area for the oxygen reduction reaction of the electrochemical reaction, so the larger the surface area of the graphite plate is, the more sites for the reduction reaction there be, which can inject more electrons and holes into the silicon area serving as the anode, thereby accelerating the etching of silicon.

In addition to the substrate surface area affects the etching results, under the same conditions, the substrate type will also affect the morphology of silicon nanostructures. Hu et al. [12] directly connect the silver-plated silicon wafers with the Au, Ag, and Pt substrates. They observed that the length and etching rate of the prepared silicon nanowire array are greatly related to the noble metal substrate used, and the order of Ag, Au, Pt is increased, as shown in Fig.3a-c, indicating that different noble metal plate
substrates have different catalytic activities during the reaction process. Substrate-enhanced metal-assisted chemical etching is used to prepare silicon nanostructure array. The experimental operation is simple, and the cost is low, a large area of silicon nanostructure array can be prepared at room temperature and pressure, the substrate used includes not only cheap and easily available graphite plate, but also noble metal plates with stable thermodynamic properties, and the etching rate increases as the increase of substrate surface area. The substrate-enhanced metal-assisted etching of silicon creates favorable conditions for large-scale industrial production of silicon nanostructure arrays.

![Fig.3 SEM morphology of enhanced metal-assisted etching of silicon by noble metal plate in aerated HF aqueous solution](image)

4. Conclusion
In this paper, taking the HF/H₂O₂/AgNO₃ two-step etching method as an example, the conventional metal-assisted chemical etching in the gas and liquid phases to prepare silicon nanostructures is introduced. We have described that using atmospheric oxygen to replace the previous nitrates, hydrogen peroxide, etc. as green oxidants, is a low-cost, environmentally friendly, simple, and efficient new technology for preparing silicon nanostructures by metal-assisted etching, and it has been proven to be feasible. In order to realize the large-area preparation of silicon nanostructures, the researchers proposed using a graphite plate as a substrate to enhance the metal-assisted etching and the mechanism of action. It was observed that the substrate and the metal film on the surface of the silicon wafer have a synergistic effect to form a galvanic cell system of the local area and through increasing the reduction of oxygen, more electron holes are injected into the silicon wafer to speed up the etching of silicon, and discussed the influence of the type of substrate and the surface area on the etching process.

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