Light-Assisted MACE Method for the Control of Silicon Nanowire Morphology

Zhaoqing Dong, Weibin Rong*, Ye Zhang and Xijun Deng

State Key Laboratory of Robotics and Systems, Harbin Institute of Technology, Harbin 150001, China

*Corresponding author e-mail: rwb@hit.edu.cn, 16S008065@stu.hit.edu.cn, 1726654667@qq.com, dxj@boshi.cn

Abstract. As a kind of one-dimensional nanostructure, silicon nanowires have a very wide range of applications in photovoltaic devices, electrical devices, and biosensors. The morphology control of nanowire arrays greatly affects the performance of nanowire arrays. In this paper, we introduce the light-assisted MACE method to prepare nanowire arrays. Through a large number of experiments, the effects of different light intensities and light wavelengths on the morphology of the formed silicon nanowire arrays are analyzed. At the same time, the degree of aggregation of nanowires is taken as the characterization parameter of the morphological characteristics, the change rule of clustering density and the change rule of the etching rate under different illumination power and wavelength conditions are qualitatively analyzed. Finally, we make a preliminary exploration and analysis of the reasons for this appearance.

1. Introduction

Silicon nanowires not only have the special properties of semiconductors, but also have some physical properties, such as visible photoluminescence, field emission and thermal conductivity, which are different from the bulk silicon materials [1-3]. Furthermore, the silicon nanowire array has excellent light trap ability that can improve the performance of the solar cell. Therefore, it has fascinating properties and application in a wide range of areas, such as optoelectronic devices, new energy and biology/chemistry sensors, etc [4-6]. The preparation of corresponding silicon nanowires according to the topography has become an important research topic, and a great deal of research has been conducted on the control of the morphology of the nanowires. Several methods of shape control have been developed at present, including surface tension control of the morphology of curved silicon nanowires [7], capillary force control methods [8], and HF/H2O2 ratio control methods [9].

The principle of surface tension methods and capillary force control methods is that after the preparation of nanowires, the surface tension of the liquid on the surface of the sample will exist in the evaporation process. This force can produce the function of self-assembly at the micron level, thus achieving the effect of controlling the morphology of nanowires. This method is based on accurate control of the location of nano column. Although the method is relatively simple, the required equipment and experimental environment are relatively high [8]. Another methods to control the morphology of the nanowire array is adjusting the ratio of HF/H2O2 in the MACE reaction solution. It is not difficult to change the ratio of the solution, but this method has a great influence on the etching rate, and it is...
difficult to realize real-time control [10]. Compared with the two methods, this paper will focus on the analysis of nanowire morphology regulated by light-assisted MACE. The process of this method is simple, the parameters of the laser are easy to control and the cost of the required equipment is low. This method can simply and efficiently produce nanowire arrays with a given morphology.

2. Experimental Mechanism

The light-assisted MACE etching principle and experimental apparatus are shown in Fig. 1. Under the irradiation of laser, a Schottky barrier is generated in the contact area between the silver nanoparticles and the silicon substrate, and silver nanoparticles are deposited on the surface of the monocrystalline silicon. The silicon substrate with the silver film attached is placed in the etching solution to react. At this time, the area of the silicon substrate covered with silver particles is etched into the hole, and the area not covered with silver particles is hardly etched. Finally, an array of nanowires with a relatively long diameter is formed. The frequency and light intensity of the laser introduced in this experiment can be adjusted; the silicon wafer used is an N-type single-throw silicon wafer with a crystal orientation of \( <111> \) and a resistivity of 0.005 \( \Omega \cdot \text{cm} \). The silicon wafer was cut into a \( 10 \times 10 \text{ mm}^2 \) sample, ultrasonically cleaned for 90 minutes and then placed in hydrofluoric acid for immersion. The light source was adjusted to a specified power and wavelength, and the treated silicon wafer was placed in a mixed solution of \( \text{H}_2\text{O}, \text{HF} (40\%) \) and \( \text{AgNO}_3 \) (0.05 mol/L) in a volume fraction of 5:1:1 for 3 minutes. The silver nanoparticles can uniformly adhere to the surface of the monocrystalline silicon to form a silver layer. Then, the sample was washed with water, and etched in a mixed solution of \( \text{H}_2\text{O}, \text{HF} \) and \( \text{H}_2\text{O}_2 \) (30\%) in a volume fraction of 9:8:1 for 30 minutes, and then cleaned with deionized water. Finally, the residual silver particles on the surface were removed with dilute nitric acid and placed in a storage box for observation.

3. The formation and characterization of new morphologies.

Removing the illumination in the experimental method is a traditional MACE method. The obtained nanowire arrays are evenly distributed and the nanowires are vertical and of equal length, as shown in Fig. 2 (A) and (C): The length of the nanowires is approximately 4.56 \( \mu \text{m} \), the diameter is about 200nm. After adding light into the MACE system, the nanowire array produces a significant change in morphology. The vertically and uniformly dispersed nanowire arrays appear tilted and converged, and the length of the nanowires is also varied. As shown in Fig. 2 (B) and (D).
Figure 2. Nanowire morphology prepared by traditional MACE method and optically assisted MACE method

We need to characterize the degree of aggregation of silicon nanowire arrays and propose new calibration methods. It can be clearly seen from the SEM plot that the brightness of the nanowires is significantly greater than that of other places, so the area of the bright regions of the SEM can be used to characterize the degree of nanowire aggregation. First select the area A of the same size, set the specified gray level threshold to binarize the image, and then convert the binarized image into a matrix. We can calculate the total number of non-zero elements in the matrix S, denoted as the total area of the bright of the picture. We define the clustering density as a physical quantity that reflects the degree of nanowire aggregation, and clustering density=S/A. In the case of relatively uniform etching, the concentration of nanowires can be accurately reflected, which helps to qualitatively analyze the aggregation of silicon nanowires and the trend of changes with external conditions. Obviously, the larger the clustering density is, the higher the degree of nanowire aggregation is, and the smaller the clustering density is, indicating the lower the concentration of nanowires.

Figure 3. SEM image and binarized image

4. The effect of light intensity on morphology of nanowires
In order to ensure uniform initial conditions, the wavelength of laser is fixed at 700nm, and the optical power are set to 5W and 10W. The nanowire morphology obtained in the experiment is shown in Fig. 4(B) and (C). Compared with the case of no light for the silicon nanowires (Fig. 4 (A)), a very significant change in morphology occurred, and the silicon nanowire arrays changed from a substantially vertical ordered array to a tilted and aggregated silicon nanowire array. According to the method for calculating the degree of aggregation calibrated above, after binarizing the SEM plot, it can be seen that the degree of aggregation also decreases as the light intensity increases.
In order to qualitatively describe this morphology change, the degree of nanowire aggregation was measured under as much optical power as possible for analysis. The required laser power values are 0W, 2W, 4W, 6W, 8W and 10W. The etched SEM images are binarized and calculated according to the previously defined method. The result is shown in Fig. 5 (A), the clustering density rapidly decreases in the initial illumination power range (0-4W), and the decreasing trend becomes gentle with the increase of the optical power. This means that when the optical power changes from 0 to 4 W, the degree of aggregation of the nanowires increases rapidly, and this increase tends to slow down as the optical power increases. In addition, we should note that as the optical power increases, the silicon nanowires' colony heads tend to form similar to the "melted" topography. At the same time, we also analyzed the etching rate of silicon nanowires as a function of optical power intensity. As shown in Fig. 5(B), when the illumination power increases from 0 to10W, the length of the silicon nanowires increases from 4.6μm to 8.8μm, which is approximately a linear increase. Experiments show that the illumination can accelerate the etching rate.

5. The effect of wavelength on morphology of nanowires
Previous experimental results have shown that illumination power or the number of photons has an important influence on the morphology of silicon nanowires. This naturally leads to the question of whether the photon energy will also affect the morphology of the silicon nanowires and what effect it will have. First, we fixed the initial conditions of the experiment: the optical power was fixed at 5 W. We selected five wavelengths for the study: 950 nm (infrared light), 650 nm (red light), 532 nm (green

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Influence of illumination power on the formation of Si NWs. (A) (D) No illumination. (B) (E) 5W illumination power. (C) (F) 10 W illumination power.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{(A) Clustering density versus illumination power \hspace{2cm} (B) Length of Si NWs versus illumination power.}
\end{figure}
light), and 365 nm (ultraviolet light). As shown in Fig. 6 (A), (B) and (C), changing the wavelength (or photon energy) of light also has an important effect on the formation of silicon nanowires. Under the condition that the wavelength of the irradiation light is infrared (wavelength of 950 nm), the formed silicon nanowires have only a slight inclination and the shape of the aggregation is not obvious, which is very similar to the case of no illumination. When the photon energy rises to a wavelength of 650 nm, the tilt and aggregation of silicon nanowires become more and more obvious, and the silicon nanowires are bent. This trend became more obvious in the case of green light (532 nm) irradiation. Experiments show that when the light wavelength is adjusted from 980 nm to 485 nm, the clustering density decreases from 24.1 K.mm\(^{-2}\) to 14.5 K.mm\(^{-2}\). However, the length of the nanowires is almost unchanged, both being 6.5 \(\mu\)m.

![Figure 6. Influence of wavelength on the formation of Si NWs. (A) 980 nm. (B) 650 nm. (C) 532 nm. (D) 365 nm; (E) Length and clustering density of Si NWs under illumination with different wavelength](image)

However, when we irradiated with ultraviolet light (365nm), we noticed a dramatic change in morphology. As shown in Fig. 6 (D), under this condition, the silicon nanowires form a short nano column with a sharp head. The length of the nanowire is about 3.1 \(\mu\)m, which is much shorter than that of the previous silicon nanowire. It is worth noting that we must consider that in this experiment, the illumination power we control is constant, and as the photon energy increases, the number of photons decreases. Using the previous experimental results, a similar change in morphology occurs when the number of photons increases. The preliminary conclusion we can obtain here is that the degree of increase in photon energy is equal to the effect of an increase in the number of photons at least. With the increase of photon energy, tilt and settlement are more and more obvious. However, in Fig. 6 (E), we find that the length of the silicon nanowires decreases with the increase of the photon energy, which is opposite to the change trend of the photon number increase. The opposite situation may be due to a decrease in the number of photons or an increase in the etching of the silicon nanowire heads.

6. Conclusion
In this paper, we introduced the method of light-assisted MACE method to control the morphology of nanowire arrays, and demonstrate the new morphology formed under different light intensities and different wavelength. We first defined the “clustering density” and used it to characterize the degree of aggregation of nanowire arrays. We also qualitatively studied the variation of the clustering density and the variation of the etching rate under different illumination power and wavelength. It was found that both the increase of the number of photons and the increase of the photon energy can strengthen the tilt and agglomeration of the silicon nanowires. While the etching rate is positively related to the number of photons, it is negatively related to the photon energy.
Acknowledgments
This work was financially supported by National Natural Science Foundation of China (No.51675141).

References
[1] Feng S Q, Yu D P, Zhang H Z, et al. The growth mechanism of silicon nanowires and their quantum confinement effect [J]. Journal of Crystal Growth, 2000, 209 (2–3): 513 - 517.
[2] Au F C K, Wong K W, Tang Y H, et al. Electron field emission from silicon nanowires [J]. Applied Physics Letters, 1999, 75 (12): 1700 - 1702.
[3] Reference to a chapter in an edited book: YUAN Z J. Nano science and technology [M]. Harbin: Harbin Institute of Technology Press, 2004: 478-495.
[4] Dai Y A, Chang H C, Lai K Y, et al. Subwavelength Si nanowire arrays for self-cleaning antireflection coatings[J]. Journal of Materials Chemistry, 2010, 20 (48): 10924 - 10930.
[5] Fan X, Guocai L I, Cheng C, et al. Progress in Controlled Fabrication Techniques and Applications of Silicon Nanowires Associated with Metal-assisted Chemical Etching [J]. Chinese Journal of Applied Chemistry, 2013, 30 (11): 1257 - 1264.
[6] Lv W, Zhang S. Controlled synthesis of Si nanowire arrays through metal assisted silicon chemical etching [J]. Semiconductor Optoelectronics, 2011, 32 (3): 363-365+397.
[7] Y.Cui, M.T.Björk, et al. Integration of Colloidal Nanocrystals into Lithographically Patterned Devices [J]. Nano Letters, 2004, 4 (6): 1093 - 1098.
[8] Duan H, Berggren K K. Directed Self-Assembly at the 10 nm Scale by Using Capillary Force-Induced Nanocohesion [J]. Nano Letters, 2010, 10 (9): 3710.
[9] Lee D H, Kim Y, Doerk G S, et al. Strategies for controlling Si nanowire formation during Au-assisted electroless etching [J]. Journal of Materials Chemistry, 2011, 21 (28): 10359 - 10363.
[10] Wang D, Ji R, Du S, et al. Ordered arrays of nanoporous silicon nanopillars and silicon nanopillars with nanoporous shells [J]. Nanoscale Research Letters, 2013, 8 (1): 1 - 9.