Effect of NaOH solution concentration on the quality of controllable silicon nanowires array fabrication

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Abstract

Ordered silicon nanowires array with large area is produced on the surface of a silicon substrate by using anodic aluminum oxide (AAO) assisted chemical wet-etching. To improve the quality and area of silicon nanowires array, the AAO whose surface is sputtered with about 15 nm thick gold nanofilm, is dissolved in NaOH solution of different concentrations. The NaOH concentration eventually affects the physical structure of the gold nanofilm floating on the surface of the solution. The higher the concentration of NaOH, the greater is the surface tension, the flatter is the gold film, the larger is the distribution area and the better is the quality of the nanowire array. However, as the concentration reaches 2.5 mol L−1, excessive surface tension seriously damages the integrity of the gold film, a happening which cannot guarantee the realization of a large area for the array. The experimental results show that NaOH concentration is one of the most important factors affecting the quality and area of silicon nanowires array. Suitable configuration of NaOH solution concentration during the fabrication process effectively increases the quality and controllable growth area of silicon nanowires array.

1. Introduction

Silicon nanowires array not only has photoelectric properties that are the same as other silicon materials but also has those photoelectric properties that are different from polished bulk silicon due to the special structure on the surface [1, 2]. The ordered structure of nanoarrays can reveal the collective effect of nanowires. The nanoarrays also have the characteristics of both the synergistic and quantum coupling effects that a single nanowire does not possess [3, 4]. The photoelectric properties of the silicon nanowires array can be regulated by controlling the size, shape, structure, and distribution of the nano unit. The template method is an important means for the synthesis of nanostructured array. Taking a template as the carrier can precisely control the morphology of materials and solve the problem of dispersion stability of materials. Anodic aluminum oxide (AAO) membranes have the benefits of insulation, adjustable pore size, low cost [5, 6], etc. It is suitable for preparing a nanoscale monodispersed arrays with uniform diameter, and the macroscopic properties of these nanomaterials can be controlled by changing the distribution and morphology of nano units [7–9].

Jungkil Kim et al from Korea Research Institute of Standards and Science developed Au/Ag bilayer metal meshes with regular hexagonal arrays of nanoholes replicated by AAO as a catalyst, and fabricated the ordered arrays of silicon nanowires array with precise control of the location, diameter, length and density [10]. Huang et al deposited noble metal meshed array on ultra-thin AAO membranes, transferred it to the silicon substrate by solution method, and prepared highly ordered silicon nanowire arrays having a diameter less than 10 nm on the silicon substrate after etching [11, 12].

Yet, these methods ignore the effect of surface tension of the solution on noble metal nanofilms, which limits the growth area of nanowires. The main task of this experiment was to find out the relationship between the surface tension of NaOH solution and the formation of nanowires. The specific experimental arrangement follows a three-step process. Initially, Gold nanofilms with about 15 nm thickness were sputtered on the surface...
of AAO by ion sputtering, and the ordered gold grids array was prepared by dissolving the AAO membrane in the NaOH solutions of different concentrations. Then, the variation trend of the surface tension coefficient with the concentration of NaOH solution was measured by the Jolly balance. Finally, the silicon nanowires arrays with different qualities and growth areas were prepared by changing NaOH solution concentrations after etching, and the mechanism of the effect was explained.

2. Experiment

2.1. Gold nanofilm transferring and Si nanowires wet-etching

To obtain gold nanofilm with the same structural shape as the AAO, gold nanofilms of about 15 nm thickness were sputtered (sputtering current: 3 mA; sputtering time: 220 s) by ion sputtering coater (SBC-12, KYKY Technology, Beijing, China) on the surface of the AAO [13, 14]. The working principle of ion sputtering coater is physical vapor deposition. That is, when the target material is bombarded by ions, the atoms on the surface of the target material will sputter, promoting the controllable transfer of atoms from the source material to the sample. Then the AAO coated with gold film was immersed in NaOH solution. Within about 2 to 18 min, as the AAO gradually got dissolved, the gold nanopore array needed in the experiment floated on the surface of NaOH solution. Then it was transferred to a cleaned silicon wafer, as shown in figure 1.

The chief component of AAO is amorphous Al2O3. The chemical equation for NaOH reacting with AAO is as follows.

\[
\text{Al}_2\text{O}_3 + 2\text{NaOH} = 2\text{NaAlO}_2 + \text{H}_2\text{O}
\]  

(1)

With the increase in NaOH concentration, the reaction is easier to proceed with. The dissolution times of AAO by NaOH solutions with different concentrations are shown in table 1.

| Concentration  | 0.625 mol l⁻¹ | 1.25 mol l⁻¹ | 1.875 mol l⁻¹ | 2.5 mol l⁻¹ | 3.125 mol l⁻¹ |
|---------------|---------------|--------------|---------------|-------------|---------------|
| Dissolution time | 17'52"       | 11'20"       | 6'38"         | 4'49"       | 2'36"         |

Subsequently, the silicon substrates with gold films are placed in the etching solution H2O2: HF: H2O = 5: 12: 37 (40 wt% HF, 30 wt% H2O2) for 60 min.

2.2. Surface tension of NaOH solutions

A layer of taut membrane is formed on the surface of liquid due to the interaction between solvent molecules and the solute molecules. The surface of the membrane has tension called surface tension of the solution [15, 16]. The methods for measuring the surface tension coefficient of solutions usually include pulling escape, capillary elevation, and droplet weighting method, etc [17]. The surface tension coefficient of NaOH solution is measured by pulling escape with new type FB737 Jolly balance, and its diagram is shown in figure 2.

The NaOH solutions of different concentrations were injected into the cleaned beaker. A metal ring was used as the contact body with the liquid surface. Keeping a level state of the metal ring, the liquid surface was controlled by the lifting platform. The metal ring in the horizontal position, was slowly immersed into the solution to be determined, by rotating the lifting knob. When the metal ring left the solution surface, a layer of membrane was formed in the middle of the ring. Considering the gravity of the metal ring as \( m_0 \), the upward tensile force as \( F \), and the surface tension of the liquid as \( f \), the three parameters form the relationship:

\[
F = (m + m_0)g + f
\]  

(2)
where, \( m \) is the mass of solution film, \( m = m_0 \), and the surface tension is proportional to the circumference of the contact surface, as shown below:

\[ \alpha = \frac{F}{d} \]

where \( \alpha \) is the surface tension coefficient, \( d \) is the metal ring diameter, from which the following formula is derived:

\[ \alpha \approx \frac{F - m_0 g}{\pi d} \]

When the metal ring was immersed into the liquid, the position value of the lower end of the spring became \( S_1 \). When the metal ring was slowly pulled up, the liquid film broke down instantaneously, and the reading of the lower end of the spring became \( S_2 \).

\[ F - m_0 g = K (S_2 - S_1) \]

where \( K \) is the stiffness coefficient of the spring. The stiffness coefficient of spring was measured as \( K \approx 0.710 \text{ N m}^{-1} \).

### 3. Results and discussion

#### 3.1. Surface tension coefficient of different concentrations of NaOH solution

According to formula (7), the surface tension coefficients of NaOH solution with different concentrations at room temperature can be obtained.

The measured values of \( d = 10.5 \text{ cm} \), \( S_1 \) and \( S_2 \) are shown in table 2.

Substituting the values from table 2 into formula (7), the relationship obtained between the surface tension coefficient and concentration of NaOH solutions is shown in table 3 and figure 3.

NaOH belongs to the category of non-surface-active substances, and the surface tension coefficient of the solution obviously increases with the increase in solution concentration. Ions of these substances undergo hydration reaction, and the concentration of non-surface-active substances on the surface becomes lower than that in the interior \([18, 19]\). There are numerous factors affecting the surface tension coefficient of solutions, such as the type of solvent, the concentration of solute, temperature of solution and the impurities contained in a solution \([20, 21]\).

Gold films float on the surface layer of the solutions which act as the interface between gas and the liquid phase. The forces acting on the surface layer molecules of the solvent are different from those acting on the...
The internal molecules of the solvent remain symmetrical under the forces from adjacent molecules, which remain in an equilibrium state. In this state, the molecular spacing is nearly the same as the molecular diameter. Consequently, the resultant force of the solvent molecules in all directions is close to zero. On one hand, surface layer molecules are affected by the gas molecules from above, and on the other hand, by the solvent molecules from the bulk. The attraction of the upper gas molecules is less than that of the bulk solvent molecules. Hence, the symmetry of the force on the molecules on the surface layer of solvent is destroyed, and the resultant force is not zero. The direction of the resultant force is perpendicular to the interior of the solution, resulting in a tendency of automatic shrinkage of the liquid surface, as shown in figure 4. Hence, the gold nanofilm floating on the surface of sodium hydroxide acts like a tight rubber film.

From the viewpoint of energy, the internal energy of the solution is mainly expressed as molecular kinetic energy, and on the surface layer of the solution, both kinetic and potential energies exist simultaneously. The molecules on the surface layer are affected by the internal attraction of the liquid, and move in the same direction along with the internal attraction, as the potential energy decreases. The molecules on the surface layer of solution have more potential energy than those in its interior, which makes the spacing of molecules larger, their distribution sparser and the density of the molecules lower. The gold nanofilms floating on the surface of the solution are attracted by the stronger forces inside the solution because of the increase in NaOH.

| Concentration (0.625 mol l⁻¹) | 0.625 mol l⁻¹ | 1.25 mol l⁻¹ | 1.875 mol l⁻¹ | 2.5 mol l⁻¹ | 3.125 mol l⁻¹ |
|-------------------------------|--------------|--------------|--------------|-------------|--------------|
| Surface tension coefficient (10⁻²N·m⁻¹) | 69.99 | 71.9 | 73.83 | 75.16 | 77.65 |

Figure 3. The relationship between the surface tension coefficient and concentration of NaOH solution.

Figure 4. The distribution of the surface layer molecules and internal molecules.
concentration, and it shrinks to a certain extent, even to the point of having the tendency to sink. At this point, it becomes difficult for the gold nanofilms to be completely transferred to the silicon wafers.

3.2. The surface tension of NaOH affecting the morphology of gold nanofilms

Table 1 shows that the increase in NaOH concentration accelerates the dissolution rate of AAO. When the concentration of NaOH solution is too high (> 1.875 mol l\(^{-1}\)), and the dissolution rate of AAO is too fast (< 5 min), AAO is prone to bending deformation. The physical structure of gold film attached to AAO gets easily affected by changes in the surface tension. After dissolving AAO into NaOH solutions of different concentrations, a scanning electron microscope (SEM, SU1510, Hitachi, Tokyo, Japan) was used to observe the microstructure of gold nanofilms transferred to silicon substrates.

As shown in figure 5, NaOH solutions of 0.625 mol l\(^{-1}\) and 1.25 mol l\(^{-1}\) make most regions of gold nanofilms show better smoothness and integrity. NaOH solution of 1.875 mol l\(^{-1}\) caused partial damage to the gold nanofilm, resulting in small holes. The NaOH solution of 2.5 mol l\(^{-1}\) aggravated the damage of the gold nanofilm even further, wherein the holes appear more frequently and become larger.

The amplified external force might cause different degrees of plastic deformation in the inner region of gold film, and the distribution of plastic deformation is not uniform. When the gold nanofilms left the surface of the solution, that is, the external force produced by the liquid on the gold film was removed, the elastic recovery of each region of the film did not appear to be completely consistent. Consequently, some regions of the film became thinner, and in some regions small cracks or even fractures appeared, as shown in figure 6.

Different surface tensions of different solutions stretch the gold nanofilms floating on the surface of the solution to different degrees. Gold nanofilm has excellent extensibility, and as can be seen in the figures 6(c) and (d), the broken gold meshes are drawn into filaments, yet connected. Gold, which generally does not react with strong acids and bases, was chosen as the catalyst in the etching process, mainly because of its stable chemical properties. Therefore, the changes in NaOH concentration have no chemical effect on the gold nanofilm itself, but only on the force exerted on the gold nanofilm.
3.3. The growth of silicon nanowires array

The growth of silicon nanowires array is also one of the important factors to be considered in the etching process. When the adhesion of the contact surface is not strong enough, the gold nano-film will fall off the surface of the silicon wafer and cannot be used as an etching template. There are numerous factors affecting adhesion. The most fundamental experimental procedure is to clean the silicon substrate thoroughly. Any contamination of the layer on the surface of the substrate saturates the chemical bonds, and the removal of the contaminated layers can improve the adhesion of the contact surface.

In the process of sputtering, the deposition rate of the gold film should be taken into account. The rate of adhesion decreases with the increase in deposition rate since the structure of gold nano-film is loose and the adhesion is poor. But, the structure of the gold nano-film is too hard to be used as a catalyst to penetrate into the space formed by the etched Si. As a result, the sputtering time of 220 s and sputtering current of 3 mA were determined by repeated experiments [13].

Four samples coated with gold nanofilms were placed in the etching solution H₂O₂: HF: H₂O = 5: 12: 37 (40 wt% HF, 30 wt% H₂O₂) for 60 min [13]. The microstructure of silicon nanowires array as observed by SEM, is shown in figure 7.

Gold nanogrid arrays not only act as catalysts in the etching process but also provide a template for the growth of nanowires. The etching reaction mechanism is shown in figure 8 [24, 25].

(1) Because of the catalytic activity of noble metal particles, the oxidant (H₂O₂) accelerates the decomposition, thereby generating holes.

(2) The holes are transported to the silicon/noble metal junction by metal particles.

(3) The silicon wafer at the silicon/noble metal junction is oxidized preferentially by injected holes to produce SiO₂, as represented by equation (8).

\[
\text{Si} + 2\text{H}_2\text{O}_2 \rightarrow \text{SiO}_2 + 4\text{H}^+ + 4\text{e} \quad (8)
\]
A part of the holes is consumed at the silicon/metal junction, and then SiO$_2$ reacts with HF to form a water-soluble silicate. That is, the Si in contact with the metal is etched much faster compared to a bare Si surface without metal coverage, as represented by equation (9).

$$\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \quad (9)$$

The excess holes may diffuse to the sidewalls and surface of the nanowires, resulting in secondary etching.

With the uninterrupted sinking of gold particles, the areas not covered by gold on the substrate form numerous tiny columnar structures conformal with the gold nanogrids, which acts as the silicon nanowires array [26–28]. For the sample made from AAO dissolved in 0.625 mol l$^{-1}$ NaOH, the nanowires appear mainly at the boundary of the gold nanofilm and form a small area. For the samples made from AAO dissolved in 1.25 mol l$^{-1}$ and 1.875 mol l$^{-1}$ NaOH, nanowires are still produced from the boundary of the gold nanofilm.
With the increase in solution concentration, the coverage area of nanowires gradually increases. The reason for this phenomenon may be the enhancement of solution surface tension which makes the gold nano film to stretch, thereby changing its length and thickness. The physical structure of the gold nano film at the boundary is more suitable for penetration as a catalyst. According to the above observation, the area of an array formed by AAO dissolved in 2.5 mol l\(^{-1}\) NaOH solution should be the largest among the four samples. Yet, the surface tension of the solution is too strong to damage the gold nanofilm extremely, and the nanowires don’t form in a large area. As a result, there is no linear relationship between the concentration of NaOH solution and the area of formation of nanowires, and the balance between these was considered in the experiment. According to the analysis of the current experimental results, the surface tension of 1.875 mol l\(^{-1}\) NaOH solution makes the gold nanofilm floating on its surface display better uniformity and integrity in the same sputtering parameters as other three samples. Nanowires start to grow from the boundary and expand continuously to the interior of the gold nanofilm, and the coverage area of the nanowires is the largest among the four samples. The stereogram of nanowires observed by SEM is shown in figure 9.

4. Conclusion

In this paper, AAO membranes were used as a master template to replicate the gold nanofilms. Combined with chemical wet-etching, the ordered silicon nanowires array is prepared on the surface of a silicon substrate through the catalytic action of gold. At room temperature, we demonstrated that the surface tension of NaOH solution with different concentration affects the scale and quality of silicon nanowires array. The etching results showed that when the concentration of NaOH solution is less than 1.875 mol l\(^{-1}\), the silicon nanowires start to grow from the boundary of the gold nanofilm, and the coverage area of array is gradually expanded to the interior of gold nanofilms. When the concentration of NaOH solution is up to 2.5 mol l\(^{-1}\), the gold nanofilm is seriously damaged due to the enhancement of internal stress in the solution. Although nanowires are formed in the area covered by gold nanofilm, it cannot be realized in a large area. Proper configuration of NaOH solution concentration effectively increases the growth area of controllable silicon nanowires array.

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