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Formation kinetics and structures of high-density vertical Si nanowires on (111)Si substrates

S. L. Cheng^{a,b,*}, C. H. Chung^a and Y. H. Chang^a

^aDepartment of Chemical and Materials Engineering, National Central University, Chung-Li City, Taoyuan, Taiwan, Republic of China ^bInstitute of Materials Science and Engineering, National Central University, Chung-Li City, Taoyuan, Taiwan, Republic of China

We report here the first study of formation kinetics of high-density vertical Si nanowire arrays formed on (111)Si substrates in aqueous AgNO₃/HF etching solutions. From TEM and electron diffraction analyses, the as-prepared Si nanowires were determined to be perfectly single crystals and the axial orientation of the Si nanowires was identified to be parallel to the [111] direction, which was identical to the orientation of the (111)Si wafers used. The typical widths of the Si nanowires prepared are in the range of 25-150 nm. The lengths of the Si nanowires were found to increase linearly with the reaction time in samples treated at 5-30 °C. By measuring the growth rate at different temperatures, the activation energy for the linear formation of Si nanowire arrays on blank-(111)Si was obtained from an Arrhenius plot to be about 0.38 eV. The results of the contact angle measurements further indicated that the hydrophobicity of the Si samples was enhanced significantly by the formation of Si nanowire arrays. The hydrophobic behavior of the HF-treated Si nanowire arrays could be explained by Cassie's model.

Key words: Formation kinetics, Silicon nanowires, Electrochemical synthesis, Hydrophobicity.

Introduction

One-dimensional (1D) semiconductor nanostructures, such as nanorods, nanowires, and nanotubes, have attracted increasing interest in recent years because they are expected to play an important role in the applications of advanced nanoelectronic devices, chemical and biological sensors [1, 2]. Among these 1D nanostructures, silicon nanowires (SiNWs) possess excellent physical properties and considerable technological promise, which make them the ideal building blocks for designing next generation electronic nanodevices [3, 4]. To date, a variety of synthesis techniques including electron beam lithography [5], laser ablation [6], oxide-assisted growth (OAG) [7, 8], and chemical vapor deposition [9, 10] have been routinely used to synthesize large-scale Si nanowires. However, the application of these techniques is limited by the long processing time, high operating temperature, and the complex equipment and hazardous experimental procedures employed. Recently, an alternative low-temperature synthetic route which is based on a metal-assisted chemical etching process has been proposed to overcome the above-mentioned limitations [11-14].

Using this easy method, large-scale Si nanowires with a desirable crystallographic orientation can be readily produced on Si substrates via a redox reaction between silicon and silver ions in an aqueous solution containing silver nitrate (AgNO₃) and hydrofluoric acid (HF). Recent studies

have also demonstrated that various functional Si nanowire structures have been successfully fabricated on Si substrates by this metal-nanoparticle catalytic etching technique [15, 16]. On the other hand, the surface-wetting properties of nanostructured materials were reported to be significantly affected by the surface morphologies and roughnesses [17, 18]. However, issues related to the formation kinetics and surface-wetting behavior of Si nanowire arrays prepared under different etching conditions have not been intensively studied. Since the kinetic data and surface morphologies are crucial for a basic understanding of the electrochemical synthesis process and surface wettability of Si nanowires, it is of much importance to investigate further the formation kinetics and structures of Si nanowire arrays produced on Si substrates under different experimental conditions.

In the present study, we show the successful synthesis of length-tunable vertically-aligned Si nanowire arrays on (111)Si substrates in aqueous AgNO₃/HF solutions. The surface morphologies, crystal structures, formation kinetics, and wettabilities of the Si nanowire arrays on the (111)Si substrate samples after different reaction temperatures and time are discussed.

Experimental Procedure

Single crystal, p-type (111) oriented silicon wafers with a resistivity of 1-30 Ω -cm were used in this study. The (111)Si wafers were cut into small pieces for systematic etching experiments. These blank-Si specimens were cleaned chemically by a standard procedure followed by dipping in a dilute HF solution to remove the native oxide layer. Then, the cleaned Si substrates were immediately

^{*}Corresponding author:

Tel : +886-3-4227151(ext: 34233) Fax: +886-3-2804510

E-mail: slcheng@ncu.edu.tw

immersed into the chemical etching solution contained in a Teflon beaker. The etching solution consisted of $0.02 \text{ M} \text{ AgNO}_3$ and 5 M HF. To investigate the formation kinetics of Si nanowires, the Teflon beaker was covered so as to minimize evaporation and placed in a glass vessel half-filled with water and then treated at 5-30 °C for 15-60 minutes. Following the synthesis process, the samples obtained were rinsed using deionized (DI) water and dried with dry N₂ gas. Subsequently, these samples obtained were washed in a nitric acid (HNO₃) aqueous solution bath to remove the capped Ag dendritic films and then rinsed in DI water and blown dried in the same way as above.

Scanning electron microscopy (SEM) was carried out with a Hitachi S-3000H SEM operating at 15 kV to examine the lengths and surface morphologies of the Si nanowire arrays fabricated on (111)Si substrates at various reaction temperatures and for various times. A JEOL JEM2000FXII transmission electron microscope (TEM) operating at 160 kV and selected-area electron diffraction (SAED) analysis were utilized to examine the microstructures and determine the crystallographic orientations of the Si nanowire arrays were characterized using water contact angle measurements at room temperature. Prior to the measurements, the Si nanowire samples were dipped in a dilute HF solution to remove the native oxide layer. Unless otherwise mentioned, the volume of each water droplet was fixed at 5 μ L.

Results and Discussion

Fig. 1(a) is a typical cross-sectional SEM image of the as-synthesized sample showing that the etched Si substrate was covered with a Ag layer. From high magnification SEM observations, as shown in the inset of Fig. 1(a), the Ag film was composed of numerous multi-branched Ag dendrites. Under the Ag dendritic film, high-density vertical Si nanowire arrays were found to form on (111)Si substrates. In addition, many small Ag particles of several tens to hundreds of nanometers are visible at the bottom of the as-formed Si nanowire arrays. The sinking behavior of the small Ag particles during the electrochemical etching process has been found to play an important role in the formation of vertical Si nanowire arrays. The detailed formation mechanisms of the Si nanowires formed in the AgNO₃/HF mixed aqueous solution have been comprehensively reported elsewhere [14, 19]. The wrapped Ag dendrites and nanoparticles can be completely etched away using a HNO₃ solution. Fig. 1(b) shows a typical cross-sectional SEM image of the vertically-aligned Si nanowire array after removing the Ag dendrites and nanoparticles. It is worthwhile to note that after removal of the Ag dendritic films from the sample surfaces, the Si nanowire samples obtained exhibited a dark black color. Examples are shown in Figs. 1(c)-(d). This observed color change phenomenon can be attributed to the light absorption and/or scattering by the Si nanowire arrays.

Further structural and crystallographic characterizations

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Fig. 1. Typical cross-sectional SEM images of (a) an assynthesized Si sample and (b) Si nanowire arrays on (111)Si substrate after removing the Ag dendritic film. The inset in (a) is a high-magnification SEM image of tree-like Ag dendrites grown on the surface of Si nanowire arrays. Optical photographs of the Si substrates (c) before and (d) after the formation of Si nanowire arrays (Ag dendrites have been removed).

of the Si nanowires were performed by TEM and SAED. Figs. 2(a)-(b) show representative bright-field TEM images of the Si nanowires scratched from the (111)Si substrates. The typical widths of the Si nanowires were observed to be in the range of 25-150 nm. The insets in Figs. 2(a) and (b) are the corresponding SAED patterns with the [110] and [112] zone axes of single-crystal silicon, respectively. Based on the analysis of SAED patterns, it can be concluded that all the Si nanowires produced were single crystals and the formation direction of the Si nanowires was along the [111] direction, which was identical to the orientation of the (111)Si wafers used. For the Si nanowire arrays prepared from (111)Si substrates in the etching solution at 5-30 °C for different periods of time, the evolution of the Si nanowire length



Fig. 2. (a) and (b) bright-field TEM images of the as-synthesized Si nanowires obtained along the $[1\overline{10}]$ and $[11\overline{2}]$ zone axes, respectively. The upper right insets are the corresponding indexed SAED patterns.

with reaction time was systematically examined by crosssectional SEM. Examples are shown in Figs. 3(a)-(f). As can be seen from the cross-sectional SEM images, the lengths of the Si nanowire arrays produced were observed to increase with reaction temperatures and time. The upper left insets in Fig. 3 are the corresponding top-view SEM images of the Si nanowire arrays produced. From these topview SEM micrographs, it is clearly seen that the Si nanowires are tangled with each other and held together in bundles. This phenomenon could be caused by the Van der Waals interaction between Si nanowires during the drying process. Similar formation behaviors were also observed for other Si nanowire samples examined in this study.

After a series of cross-sectional SEM examinations, the lengths of the Si nanowires versus reaction time data for (111)Si substrates treated at various temperatures were obtained. Fig. 4 shows the lengths of the Si nanowire arrays as a function of the etching time with the reaction temperatures ranged from 5 to 30 °C. The relation curves shown in Fig. 4 are almost linear. From the slops of the straight lines, the formation rates of the Si nanowires produced at 5-30 °C could be estimated. Furthermore, on the basis of the observation shown in Fig. 4, we demonstrated that the lengths of Si nanowires on (111)Si substrates could be well-controlled by tuning either the synthesis temperature or the reaction time. By measuring the formation rates of Si nanowires at different reaction temperatures, an Arrhenius plot of the ln(formation rate) versus the reciprocal of the synthesis temperature shown in Fig. 5 allows us to determine the kinetic parameters quantitatively. In this study, the apparent activation energy for the linear formation of Si nanowire arrays on blank-(111)Si substrates was measured to be about 0.38 eV.

Fig. 6(a) shows a photograph of a water droplet on the surface of a HF-treated Si nanowire sample. It is interesting to note that the Si substrate with Si nanowire arrays exhibited a hydrophobic property. To examine the surface wetting behaviors of the (111)Si substrates before and after the formation of Si nanowire arrays, water contact angle measurements were carried out. For a Si substrate with a smooth surface, the measured water contact angle does not generally exceed 90°. However, as the nanowire structures were formed on the Si substrate surfaces and subsequently dipped in a dilute HF solution, the Si nanowire samples exhibited greater surface hydrophobicity with water contact angles of 130-147°. Representative optical images of contact angles of water droplets on the surfaces of HF-treated blank-(111)Si substrate and Si nanowire samples are shown in Figs. 6(b) and (c), respectively. The upper right inset in Fig. 6(c) is the corresponding top-view SEM image of the Si nanowire array. The nanostructured surface morphology is clearly evident. The observed hydrophobic behavior of Si nanowire arrays could be explained by Cassie's model [20]. When a water droplet is placed on the hydrophobic nanostructured Si surface, it is expected that the diffusion of air below the water droplet would be retarded by the presence of the bundled Si nanowire structures. Thus, a large amount of air could be trapped in the interstices of the bundled nanowire structures. According to Cassie's model, a larger amount of air trapped in the nanostructured Si substrates would lead to an enhancement of the hydrophobicity of the sample surfaces [21, 22]. Therefore, in this experiment, the hydrophobic nanostructured Si substrates resulted in higher water contact angles on the surfaces of the Si nanowire arrays compared to the smooth silicon wafer surface.

The observed results present an exciting prospect that with appropriate controls, the above low-temperature electrochemical etching scheme promises to be an effective method for the growth of a variety of large-area lengthtunable 1D nanostructures without complex lithography and suggests investigating the formation kinetics of other Si-based nanowire arrays.

Summary and Conclusions

The formation kinetics, crystal structures and surface wetting behaviors of Si nanowire arrays on (111)Si substrates prepared in an aqueous solutions of AgNO₃/HF



Fig. 3. Cross-sectional SEM images of Si nanowire arrays produced at (a)-(c) 10 °C and (d)-(f) 20 °C. The corresponding etching times were: (a), (d) 30 minutes; (b), (e) 45 minutes; and (c), (f) 60 minutes. The upper left insets are the corresponding top-view SEM images.



Fig. 4. Plot of the length of the Si nanowires versus etching time at various reaction temperatures, illustrating a linear growth rate.



Fig. 5. Arrhenius plot of the formation rate versus reciprocal of reaction temperature for the formation of Si nanowires on (111)Si substrates.



Fig. 6. (a) A typical photograph of a water droplet on the surface of a HF-treated Si nanowire sample. Representative optical images of contact angles of water droplets on the HF-treated (b) blank-(111)Si substrate (contact angle $\sim 86^{\circ}$) and (c) Si nanowire arrays formed at 20 °C for 30 minutes (contact angle $\sim 140^{\circ}$). The inset in (c) is the corresponding top-view SEM image of the Si nanowire array.

have been investigated by SEM, TEM, SAED analyses, and water contact angle measurements.

By varying the electrochemical reaction temperature and time, length-tunable vertically-aligned Si nanowire arrays have been successfully produced on (111)Si substrates. The typical widths of the Si nanowires prepared are in the range of 25-150 nm. TEM and SAED analyses clearly indicated that all the Si nanowires were single crystals and the axial orientation of the Si nanowires prepared was along the [111] direction. The lengths of Si nanowires can be controlled by adjusting the reaction temperature and time, ranging from several to tens of micrometers. By measuring the formation rate of Si nanowires at different reaction temperatures, the activation energy was obtained from an Arrhenius plot to be about 0.38 eV. From water contact angle measurements, it was found that the HF-treated Si nanowire samples exhibited greater surface hydrophobicity. The hydrophobic behavior of the HF-treated Si nanowire arrays was discussed in the context of Cassie's model.

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