Growth Mechanism of Nano-silver Wires

Yi-Feng Chiang¹, Pai-Chung Liu¹, Wei-Ting Kuo² and C.B. Lin¹*

¹Department of Mechanical and Electromechanical Engineering, Tamkang University, Tamsui, Taiwan 251, R.O.C.
²Department of Chemistry, Tamkang University, Tamsui, Taiwan 251, R.O.C.

Abstract

This study used UV-irradiated silver chloride to act as seed crystals, employed the polyol synthesis method to synthesize silver nanowires in the wide temperature range of 120 °C–176 °C, and investigated the growth mechanism of silver nanowire. The growth process of silver nanowires can be divided into three regions: region I is controlled by a mixed diffusion model involving Case I diffusion and Case II diffusion, where the activation energy needed for Case I and Case II diffusion is approximately 192 KJ/mol and 50 KJ/mol. Significant one-dimensional anisotropic growth occurs in region II, and the growth rate in this region is faster than in region I. In region III, because the {111} crystal plane of the silver nanowires has gradually been coated by PVP, the growth rate will approach saturation.

Key Words: Silver Chloride, Silver Nanowires, Kinetics, Activation Energy

1. Introduction

Transparent conducting films (TCFs) made with silver nanowires have gradually been adopted for use in touch-control screen, solar cells, and flexible displays [1, 2]. The most common methods used to manufacture silver nanowires include the template synthesis method [3, 4], seed crystal synthesis method [5, 6], and polyol synthesis [7–9]: (1) template method: Sun et al. [3, 4] used an AAO template with a thickness of 60 μm and a pore diameter of 100 nm to produce silver nanowires, and first used the AAO template to deposit a gold conducting layer 200 nm in thickness, which was placed in a mixed solution containing 18 g/L silver nitrate (AgNO₃), 120 g/L sodium citrate (C₆H₅Na₃O₇·2H₂O), 40 g/L sodium potassium tartrate (C₆H₅O₂KNa·4H₂O), and 60 g/L sodium sulphite (Na₂SO₃), and boric acid (H₃PO₃), and ammonia water (NH₄OH) used to adjust the pH to 6; electrochemical deposition was then employed to obtain silver nanowires. (2) seed crystal synthesis method: Jana et al. [5] added sodium borohydride (NaBH₄) to a silver nitrate solution, which caused the silver to be reduced to granular silver seed crystals with an average size of approximately 4 nm, which constituted solution A; sodium citrate (Na₃C₆H₅O₇) was added as a protective agent during the process of seed crystal synthesis, and prevented the granular silver seed crystals from aggregating. Solution B, which contained silver nitrate, a reducing agent (ascorbic acid), sodium hydroxide (NaOH), and a surfactant (CTAB) was then prepared, and solution A was added to solution B, causing the silver nanowires to grow. This method relies on granular silver seed crystals as nucleation points, and allows a surfactant (CTAB) to adsorb on the faces of the silver seed crystals. Because some of silver’s specific crystal faces have relatively good adsorption ability, growth of silver atoms on these faces will be blocked, which will cause the silver nuclei to grow anisotropically. In the seed crystal synthesis method, the temperature, surfactant, solution concentration, and reaction time will all affect the shape and aspect ratio of the silver nanowires. Pietrobon et al. [6] prepared a mixed solution containing 0.5 mL sodium citrate (0.05 M), 0.5

*Corresponding author. E-mail: cblin@mail.tku.edu.tw
mL polyvinylpyrrolidone (PVP, 0.05 M), 0.05 mL L-arginine (C<sub>6</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>, 0.005 M), 0.2 mL silver nitrate (0.005 M), and 7 mL deionized water, added 0.08 mL sodium borohydride (0.1 M), and stirred the solution until it turned bright yellow, which yielded decahedral silver seed crystals with a diameter of 35–45 nm. The solution was then placed under a 400 W metal halogen lamp, and illuminated with blue light for 2–5 hours using an optical filter. The decahedral silver seed crystal solution was washed in a centrifuge, which replaced the original solution with 1 mL deionized water. The next step was to stir 0.4 mL sodium citrate (0.05 M), 0.066 mL PVP (0.05 M), 2 mL deionized water, and 1 mL decahedral silver seed crystals evenly and heat to 95 °C. Maintaining this temperature, silver nitrate was then added to produce silver nanowires; the length of the silver nanowires depends on the amount of silver nitrate. (3) polyol synthesis method: Sun et al. [7] used a pump with two channels to simultaneously add 3 mL of an ethylene glycol solution (0.1 M) containing silver nitrate and 3 mL of an ethylene glycol solution (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>, 0.6 M) containing PVP (polyvinylpyrrolidone) to a 5 mL ethylene glycol solution at 160 °C and a rate of 0.3 mL/min. The resulting solution was stirred for 60 min. Because ethylene glycol has reducing ability at high temperatures, under the influence of a protective agent PVP (polyvinylpyrrolidone), the reduced silver atoms grew in the form of silver nanowires. Sun et al. [8] used ethylene glycol as a reducing agent at a constant temperature of 160 °C, and dissolved platinochloride in the ethylene glycol. Because ethylene glycol possesses reducing ability at high temperatures, the platinum ions in solution were reduced to granules approximately 5 nm in size. Because platinum and silver both have a face-centered cubic (FCC) crystal structure, and extremely close lattice constants, the platinum nanoparticles could be used as seed crystals for silver nanowires. Silver nitrate and the protective agent (PVP) were then added to grow anisotropic silver nanowires. Korte et al. [9] heated 5 mL ethylene glycol to a temperature of 151.5 °C for 1 hr while rotating at 260 rpm, and then added copper chloride (CuCl<sub>2</sub>·2H<sub>2</sub>O (99.999%)), copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (99.999%)), and cuprous chloride (CuCl (99.995%)), heated the solution for 15 min., 1.5 mL ethylene glycol solution containing PVP (0.147 M), and 1.5 mL ethylene glycol solution containing silver nitrate (0.094 M) was added. The addition of copper (I) or copper (II) chloride to the reaction in this method caused the formation of seed crystals at the start of the reaction, which reduced silver ion concentration, and removed adsorbed oxygen from the surface of the seed crystals. This caused the oriented growth of the silver nanowires. Because the oxygen molecules that were present adsorbed on and decomposed the silver seed crystals at the start of seed crystals formation, and because copper (I) quickly removed the adsorbed oxygen atoms (O<sub>a</sub>), the copper (I) was oxidized to copper (II), and the ethylene glycol (EG) could reduce the copper (II) back to copper (I).

This study proposes a method of synthesizing silver nanowires that employs UV-radiated silver chloride as the seed crystals, and using the polyether synthesis method at a reaction temperature of 120 °C–160 °C to produce silver nanowires, while also investigating the growth kinetics of the silver nanowires.

2. Experimental Steps

2.1 Production of Seed Crystals for Silver Nanowires

After placing 50 mL 0.05 M aqueous solution sodium chloride solution in an ice water bath and the solution were slowly poured into the sodium chloride solution while stirring at 300 rpm, causing silver chloride nanoparticles to precipitate. Vacuum filtration and ultrasonic washing with ethanol were then employed to produce a powder consisting of silver chloride nanoparticles with clean surfaces. The silver chloride powder was poured into 100 mL deionized water and stirred at 600 rpm until evenly dispersed. An USHIO UVL-8001M3-0 UV exposure machine was used simultaneously to irradiate the silver chloride granules for 5 min, which caused photoreduction, and caused the silver clusters to form on the surface of the particles. These were the seed crystals used to produce silver nanowires.

2.2 Production of Silver Nanowires

1 g PVP (average molecular weight of 1.3 million) was dissolved in 100 mL ethylene glycol, 0.1 g silver chloride seed crystals were poured into the solution, a magnetic stirring machine used to stir the mixture thoroughly
at 300 rpm and temperatures of 120, 130, 140, 150, and 160 °C, and 1 g silver nitrate was poured into the solution in order to produce silver nanowires. In order to understand the silver nanowire growth mechanism, samples were taken at 1, 4, 10, 20, 30, 40, 50, 60, 70, 80, 160, and 320 minutes, and the sampled silver nanowire solution washed three times in methanol to remove any unreacted solution and PVP coating the surface of the nanowires. After washing, the silver nanowire solution was poured into acetone and spun in a centrifuge at 2000 rpm for 10 min. Finally, the purified silver nanowires were removed and placed in ethanol to form a 2 w% silver nanowire-ethanol solution.

2.3 Observation of Microstructure
A Jeol JEM-2100F-HR high-resolution field emission transmission electron microscope was used to observe the morphologies and dimensions of the silver nanowires. Prior to observation, the 2 wt% silver nanowire-ethanol solution was dripped through a 400-mesh copper screen containing a carbon membrane, and the ethanol was completely separated and the powder dried. OLYMPUS OLS4100 laser scanner confocal microscope and image analysis software was employed to observe and measure the average length of the silver nanowires at different reaction temperatures and reaction times. After 2 w% silver nanowire-ethanol solution was had been through a hydrophilic silicon chip, and the ethanol completely separated and the powder dried, because the silver nanowires had unequal length, the average length of the silver nanowires was taken as the average value obtained when the length of nanowires in different five different areas was measured and experiments of each temperature was repeated twice in order to lead the data more confidence.

2.4 X-ray Diffraction Analysis
A Rigaka RINT-2000 X-ray diffractometer was used to analyze the crystal phases of the silver chloride powder following UV exposure. A Cu target (λ = 0.154 nm) was used to, the operating voltage the 40 KV, the current was 30 mA, and the scanning angle was from 20° to 80°.

3. Results and Discussion

3.1 The Silver Nanowire Growth Mechanism
The results of x-ray diffraction analysis of the silver chloride granules after UV exposure were as shown in Figure 1, and diffraction peaks corresponding to silver clusters on the surface of the granules formed via photoreduction can be seen. Following UV exposure, the silver chloride granules were evenly dispersed in the ethylene glycol. Because ethylene glycol possesses reducing ability at high temperatures, the Ag⁺ in the ethylene glycol was reduced to Ag⁰. Heterogeneous nucleation of the reduced silver atoms in the silver clusters formed silver embryos. When the size of the silver embryos exceeded the critical size for formation of silver nuclei, stable silver nuclei appeared, as shown in Figure 2(a). The lattice spacing of the silver nuclei in this figure is approximately 4 Å. At this time, the Cl⁻ in the solution played an important role: apart from providing electrostatic stabilization when the silver nuclei begin to form, the Cl⁻ can also reduce the quantity of free silver ions in solution, and thereby enable the slow release of silver ions. The silver nuclei possessed various polyhedral shapes, and nuclei with a five-twinned structure formed silver nanowires, as shown in Figure 2(b)–(d). In the silver nanowire growth process, oxygen atoms on the PVP molecules form Ag-O bonds with the unsaturated bond of the silver nuclei; because the {100} crystal planes in a five-twinned structure are larger than the {111} crystal planes, the {100} planes tend to absorb more PVP than the {111} planes. As a consequence, when PVP molecules have not fully coated the {100} crystal planes, silver ions can diffuse from the {111} crystal planes and cause reductive growth, as shown in Figure 3(a), until the {100} crystal...
has been tightly coated with PVP. At that time, silver ions cannot easily diffuse into the \{100\} crystal plane, and the silver nuclei will have significantly anisotropic growth only in the \{100\} direction, typically yielding clusters of nanowires as shown in Figure 3(d). It should be noted that after the silver nanowires have been annealed at 85 °C for 5 min., surface diffusion will create local necking, as shown in Figure 3(e). After 30 min., the local necking will spread and form groups of nanospheres linked in a linear fashion, as shown in Figure 3(f).

This study employed the polyether reduction method with UV-irradiated silver chloride to create seed crystals. This approach successfully synthesized silver nanowires at a reaction temperature of 120–160 °C, and was different from the approach in the literature [8,9] in which the polyether reduction method is used to synthesize silver nanowires at a specific temperature. In other words, when UV-irradiated silver chloride seed crystals are used in the polyether reduction method to synthesize silver nanowires, synthesis can proceed in a relatively wide temperature range, which enables silver nanowires with different aspect ratios to be obtained through the use of different reaction times within the temperature range of synthesis. Furthermore, since the aforementioned studies in the literature employing the polyether reduction method add small quantities of chloride, in the form of sodium chloride (NaCl), cuprous chloride (CuCl$_2$), or cupric chloride (CuCl), as a source of trace chlorine ions, the Na$^{+1}$, Cu$^{+2}$, or Cu$^{+1}$ ions may add variables to the experimental process, which would complicate our effort to investigate the kinetics of silver nanowire growth.

3.2 The Silver Nanowire Growth Mechanism

Figure 4 shows typical examples of the silver nanowire growth process. When the temperature synthesis is 130 °C, we can see that five-twinned nuclei (as shown in

**Figure 2.** Production of nanowires via the polyether synthesis method at a temperature of 160 °C: (a) silver nuclei; (b) five-twinned nuclei; (c) enlarged view of five-twinned nuclei; (d) TEM image of the five-twinned lattice.

**Figure 3.** (a) Anisotropic growth of silver nuclei due to coating by PVP molecules; (b) \{111\} crystal plane coated by PVP molecules; (c) \{100\} crystal plane coated by PVP molecules; (d) TEM image of clustered silver nanowires; TEM images of silver nanowires after annealing at 85 °C for (a) 5 minutes and (b) 30 minutes.
Figure 4(a), have formed at a reaction time of 1 min. When the reaction time is 20 min., short silver nanowires will form, as seen from the white, linear segments in Figure 4(b). As the reaction time increases, the average length of the nanowires also increases, until growth slows and the length seen in Figure 4(f) is reached. The silver nanowire growth curves for different reaction times at different reaction temperatures (120, 130, 140, 150, and 160 °C) are shown in Figure 5(a–e), and we can see from these figures that the silver nanowire growth process can be divided into three regions: Region I: The growth rate of the nanowires (average length divided by time) is relatively slow. Because the PVP has just begun to coat the \{100\} crystal plane of the silver nanowires at this time, the silver ions can diffuse to both the \{100\} and \{111\} crystal planes, where they engage in reductive growth. In other words, both the length and diameter of the silver nanowires will grow at this time. Region II: The silver nanowires are growing at a faster rate than in region I. Because the PVP has gradually formed a tight coating on the \{100\} crystal plane, it can effectively block the silver ions from diffusing to the \{100\} crystal plane. In contrast, the \{111\} crystal plane has only a loose coating of PVP, which enables silver ions to easily diffuse to the \{111\} plane, enabling significant one-dimensional anisotropic growth. Region III: Growth of the silver nanowires slows as PVP gradually forms a tight coating on the \{111\} crystal plane, which prevents silver ions from easily diffusing to this crystal plane and sustaining growth. Growth of the silver nanowires gradually approaches saturation during this stage. Furthermore, it can be seen from Figure 6 that the silver nanowires’ growth rate increases with reaction temperature during the initial growth stage (region I), which reflects the fact that the nanowires have not yet been coated with PVP during this stage, and silver ions can readily diffuse to both the \{100\} and \{111\} crystal planes. Moreover, the diffusion rate of the silver ions increases with reaction temperature. But as the growth of the silver nanowires reaches saturation, apart from at a temperature of 160 °C, the final length of the nanowires decreases with increasing reaction temperature, and the order of the average final length is 120 °C > 130 °C > 160 °C > 140 °C > 150 °C. This is because, throughout the silver nanowire growth process, the silver ion and PVP diffusion rates increase with reaction temperature, which increases the

Figure 4. At a reaction temperature of 130 °C, LSCM images of silver nanowires after (a) 1 min.; (b) 20 min.; (c) 30 min.; (d) 50 min.; (e) 70 min.; and (f) 320 min.

Figure 5. Silver nanowire average length and reaction time gradually curves for various reaction temperatures: (a) 120 °C; (b) 130 °C; (c) 140 °C; (d) 150 °C; (e) 160 °C.
blockage of silver ions diffusing to the \{100\} and \{111\} crystal planes by PVP. As a result, the average length of the silver nanowires drops with increasing reaction temperature. The only exception to this rule is at a reaction temperature of 160 °C, when the average nanowire length is greater than at reaction temperatures of 140 °C or 150 °C. This is because the PVP used in this study has a melting point in the range of 150 °C–180 °C, and thermal activation causes the bonding between the PVP molecular chains to weaken at a 160 °C reaction temperature, which caused the PVP covering the \{111\} crystal plane to have a loose structure, and enabled silver ions to again diffuse to the \{111\} crystal plane and drive anisotropic growth.

It can be seen from the 120 °C–160 °C growth curves for the synthesis of silver nanowires using the polyethyether method that the growth kinetics in region I tends to reflect a mixed diffusion mechanism (anomalous diffusion) that is case II interface controlled and case I diffusion controlled, which can be represented as: $X \approx (Dt)^{1/2} + vt$, where $X$ is the average length of the silver nanowires, $D$ is the case I diffusion coefficient, $v$ is the case II diffusion rate, and $t$ is the reaction time. Curve fitting can be used to obtain the case I diffusion coefficient $D$ and case II diffusion rate $v$ in region I. As shown in Figure 7, because $D$ and $v$ both comply with the Arrhenius equation, we have:

$$D = D_0 \exp \left( \frac{-E_D}{RT} \right)$$  \hspace{1cm} (1)

$$v = v_0 \exp \left( \frac{-E_v}{RT} \right)$$  \hspace{1cm} (2)

where $D_0$ and $v_0$ are both constants, $R$ is the gas constant, $T$ is the absolute temperature, $E_D$ is the activation
energy needed for diffusion to control growth, and $E_D$ is the activation energy needed for interfaces to control growth. Relying on the slope when ln $D$ vs. (1/T) and ln $V$ vs. (1/T) are plotted together, we can obtain $E_D = 192$ KJ/mol and $E_V = 50$ KJ/mol. Since significant one-dimensional anisotropic growth has already been established in region II, the growth rate is faster than in region I. And because the $\{111\}$ crystal plane has gradually been coated with PVP in region III, the silver nanowire growth rate approaches saturation.

4. Conclusions

This study used UV-irradiated silver chloride to create seed crystals, employed the polyether synthesis method to synthesize silver nanowires, and investigated the effect of different reaction temperatures and times on the silver nanowire growth mechanism. The following conclusions were obtained:

1. When UV-irradiated silver chloride is used to create seed crystals and the polyether synthesis method employed to grow silver nanowires, silver nanowires can be synthesized over a relatively wide temperature range (120 $^\circ$C-160 $^\circ$C).

2. When silver nanowires are synthesized, the oxygen atoms on the PVP molecules can form Ag-O bonds with the unsaturated dangling bonds of the silver nuclei, which causes the $\{111\}$ and $\{100\}$ crystal planes of the silver nanowires form barriers to the diffusion of silver ions. Specifically, the fact that PVP coats the $\{100\}$ crystal plane faster than the $\{101\}$ crystal plane drives the anisotropic growth of the silver nanowires.

3. The silver nanowire growth process can be divided into three regions, where the growth rate in region I is controlled by a mixed diffusion mechanism involving Case I and Case II diffusion, and the activation energies required for Case I and Case II diffusion are approximately 192 KJ/mol and 50 KJ/mol. Significant one-dimensional anisotropic growth occurs region II, and the growth rate in this region is faster than in region I. In region III, because the $\{111\}$ crystal plane of the silver nanowires has gradually been coated by PVP, the growth rate will approach saturation.

4. In terms of reaction temperature, the order of the average final length of the silver nanowires is 120 $^\circ$C > 130 $^\circ$C > 160 $^\circ$C > 140 $^\circ$C > 150 $^\circ$C.

Acknowledgement

This study is sponsored by the Ministry of Science and Technology of Taiwan.

References


Manuscript Received: Jun. 27, 2016
Accepted: Aug. 28, 2016