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Fabrication and Electron Field Emission of Silicon Nanowires Synthesized by Chemical Etching

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Vertically aligned silicon nanowire arrays, which were synthesized by using a Ag catalyst deposited with magnetron sputtering and an electrochemical etching process were investigated. The thickness of the Ag catalyst affects the microstructure of aligned silicon nanowire array. Vertically aligned silicon nanowire arrays with more uniform morphology structures were synthesized with a catalyst thickness of 40 nm on a single crystal silicon wafer at room temperature. The electron field emission data showed a lower turn-on field for silicon nanowire arrays fabricated with the electrochemical etching process. The field enhancement factor of the silicon nanowire arrays is as high as 1637. These data indicate that electrochemical etching technology is a cheap and good method for fabricating vertically aligned silicon nanowire arrays for applications in field emission devices.

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I. INTRODUCTION

Since the discovery of carbon nanotubes in 1991 [1], one dimensional nanomaterials have attracted much attention owning to their novel physical, chemical, and mechanical properties resulting from their nanosize. Silicon nanowires (SiNWs) have potential application in many fields, for instance nanoelectronic devices, nanosensors, electron emission devices and so on. Many efforts have been made to investigate of the electron field emission properties of silicon nanowires, which have promising applications in field emission displays (FEDs), cold cathode electron sources and microwave devices [2–5]. In recent years, many methods, such as laser ablation [6,7], oxide-assisted growth (OAG) [8,9], thermal evaporation [10], and other methods [11–16] have been used in the preparation of SiNWs, among which the electrochemical etching method [13–16] is an excellent technology with relative simplicity, low-expense and better growth orientation.

Peng *et al.* [17] succeeded in synthesizing of well aligned and separated SiNW array by using a combination of the electrochemical etching, nanosphere lithography, and conventional physical vapor deposition. However, the average diameter of the SiNWs fabricated by Peng was as large as 200 nm. In the present investigation, well aligned and separated silicon nanowire arrays were synthesized by using chemical etching method and DC magnetron sputtering deposition. The field emission property of a vertically aligned silicon nanowire array was investigated.

II. EXPERIMENTAL DETAILS

N type (100) silicon wafers cut into a size of 1 × 1 cm^2 were employed as substrates. The silicon wafers were cleaned ultrasonically in acetone and ethanol for several minutes respectively, and were then immersed in a mixing solution of HF and H_2O_2 to remove the metallic particles absorbed on the surface and the native oxide layer. Deionized water was used to wash the samples after each procedure. The cleaned slices were put into the magnetron sputtering system to synthesize Ag catalyst films with thicknesses from 20 nm to 40 nm; the base pressure of the chamber was lower than 5 × 10^{-5} Pa. Chemical etching of the Si wafer was carried out in a mixing solution of H_2O_2/HF with a ratio of 1 : 10. The chemical etching time was about 1 hour.

Scanning electron microscope (SEM; Hitachi S-4800) was employed to characterize the morphologies of the silver catalyst film and the SiNW array. The microstructures and the orientation of nanowires were determined by using a high-resolution transmission electron microscope (HRTEM; JEOL 2001). The field emission measurement was carried out in a vacuum chamber in which

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the base pressure was lower than 3×10^{-7} Pa. The distance between the anode and the cathode was varied from 0 to 5000 μm and was controlled by using an electric manipulator. During the measurement of the field emission, a working voltage, with a range from 0 to 10 kV, was applied and the data were automatically recorded by a computer connected to the measurement system.

III. RESULTS AND DISCUSSION

Figure 1 shows surface and cross-sectional SEM images of SiNWs fabricated in the H_2O_2/HF solution for different sliver catalyst thicknesses. Figure 1 clearly shows that the morphologies of SiNWs are highly affected by the thickness of the silver catalyst film. A dense surface structure was formed on the substrate with a 20 nm silver catalyst film (Fig. 1(a)), and the SiNWs had flake shapes. When the thickness of the catalyst film was increased to 30 nm, the surfaces of the SiNWs were sparse and were not even well-proportioned SiNWs (Fig. 1(b)). The SiNWs were linked with each other. When the thickness of the catalyst film was increased to 40 nm, the more compact silver film led to the formation of separate silicon nanowires on the silicon substrate (Fig. 1(c)). The lengths of the SiNWs, which are about several microns and with good growing orientation, could be observed through the cross-sectional images in Fig.

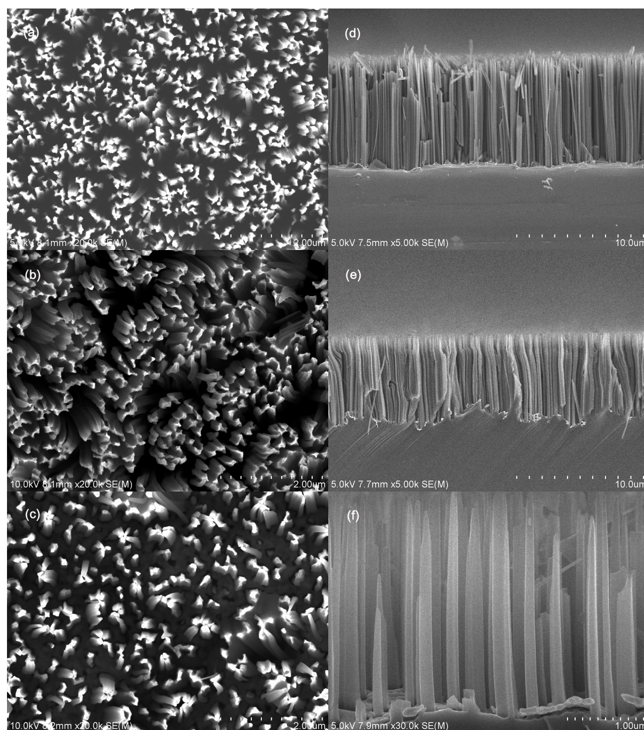

Fig. 1. (a-c) surface and (d-f) cross-sectional images of silicon nanowires fabricated with different catalyst thickness: (a) and (d) 20 nm; (b) and (e) 30 nm; (c) and (f) 40 nm.

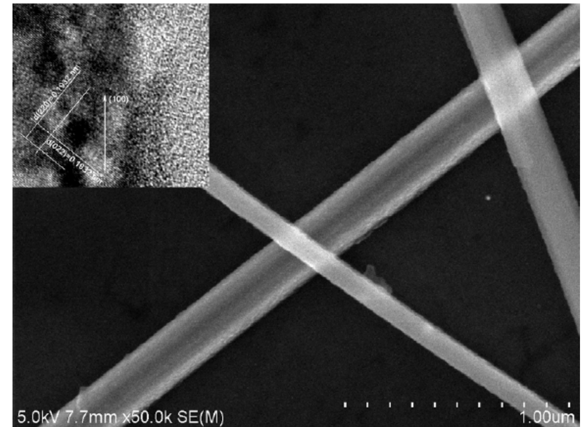

Fig. 2. Images of silicon nanowires fabricated by using chemical etching; the inset is a HRTEM image of the SiNW.

1(d) to 1(g). Figure 1 also shows that the length of the nanowires gets shorter and shorter when the thickness of the catalyst film increases from 20 nm to 40 nm.

SEM and HRTEM images (Fig. 2) show that the SiNWs with crystal structures were formed. There are single crystal structures in the core of the SiNWs and an amorphous SiO_2 layer outside of the SiNWs. The orientation of a SiNW is $< 100 >$. These clearly showed that well-aligned and uniform SiNW arrays have been fabricated on the Si substrate.

The mechanism of the SiNWs fabricated by using the chemical etching approach was first reported by Peng *et al.* [15], in which the silver catalyst film plays as the anode while the silicon substrate beneath it serves as cathode. At the end of the etching process, the silver sink at the bottom of the wafer and the silicon without catalyst on it stay to be nanowires. According to this report, the density and the shape of the silver catalyst could influence the morphology and the structure of the Si nanowire array. Figure 3 shows SEM images of the catalyst film. Considerable changes in the surface architecture can be seen. As the thickness of the film is relatively thin, the catalyst present to the shape of separating particles, and the particle sizes are not uniform. The thin catalyst particles have no catalytic activity and can not support the redox reaction. These induce more of the silicon surface not to be etched. Then, Si on the area of interstitials and thin catalyst particles are preserved, and other areas covered with silver film are corrupted during the chemical etching. At this time, flake SiNWs may be formed during the chemical etching in the H_2O_2/HF solution. With increasing thickness of the silver catalyst film, silver catalyst films with uniform surface structure are gradually fabricated on the Si substrate. Many interstitials with uniform distribution can be formed when the silver film is thicker than 40 nm. These interstitials are propitious to the formation of separating SiNWs during the chemical etching. Then, vertically aligned nanowire arrays with a separate SiNW distribution can be fabricated by using a

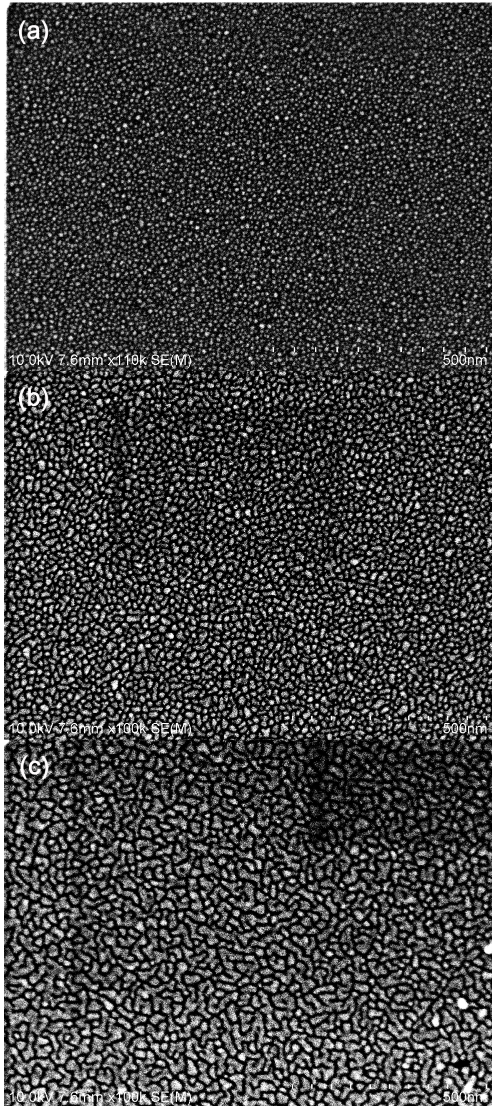

Fig. 3. SEM images of the silver catalyst with different thicknesses (a) 20 nm, (b) 30 nm, and (c) 40 nm.

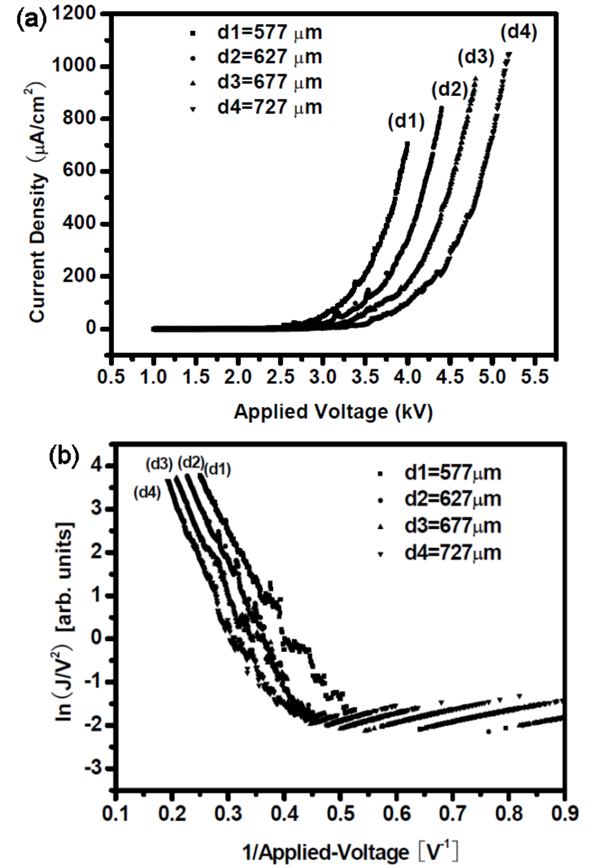

Fig. 4. Field emission properties of SiNWs with different measuring distances: (a) $J-V$ curves, and (b) $F-N$ plots.

silver catalyst film with a uniform surface structure.

Many experiments show that the SiNW is an important nanomaterial for electron emission devices [2–4]. According to the above results, chemical etching is a simple and convenient technology for the fabrication of aligned SiNW arrays. In order to understand the electron field emission characteristics of aligned SiNW arrays fabricated by chemical etching, the emission current density versus applied electrical field were determined in a diode measurement system. Figure 4 shows $J-V$ curves and Fowler-Nordheim ($F-N$) plots of the SiNW arrays. The distance between the anode and the cathode was varied from 577 μm to 727 μm. Figure 4 clearly shows that typical electron field emission curves were obtained. The turn-on field (the electric field at which the current density is equal to 10 μA/cm^2) of the SiNW array is about 4.44 V/μm, which is lower than other reported results [18]. The current density − voltage ($J-V$) curves are relatively smooth and reproducible. The field emission current density can reach as high as 1000 μA/cm^2 at a field of about 7.09 V/μm. From Fig. 4(b), a linear relationship between ln(J/E^2) and $1/E$ can be seen in the high-field region, which indicates a conventional field emission mechanism. According to the $F-N$ equation, the field enhancement factor β can be calculated by using

$$\beta = -B\Phi^{3/2}\frac{1}{S} \tag{1}$$

where $B = 6.83 \times 10^{-3}$ (eV$^{-3/2}$ V μm^{-1}), Φ is the work function of SiNWs, E is the applied field (V μm^{-1}), and S is the slope of the $F-N$ plot. We assumed that the work function of the SiNWs was 4.15 eV. The β of SiNWs fabricated by using the chemical etching technology was about 1637. At the same time, uniform shifting the $J-V$ curves for the SiNW arrays have been observed during measurement at different distance, and the voltage reached at the same field emission current density gradually increased with increasing distance. However, the slopes of the $F-N$ plots measured at different distances are similar. Which indicate that the field enhancement factor β is correlated with only the shape,

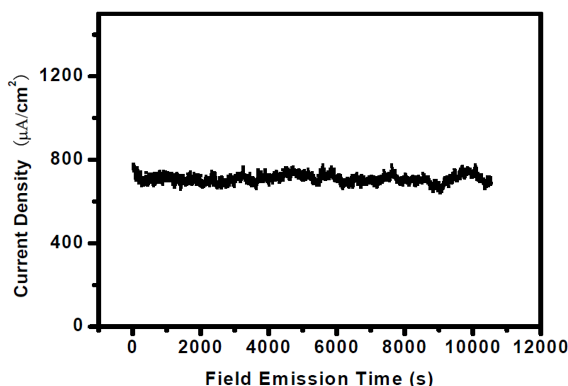

Fig. 5. Time stability of the field emission current density of the SiNW array.

the diameter and the aspect ratios of the SiNWs, but not with the measurement distance. This is completely different from the result reported by Xu *et al.* [19], in which the field enhancement factor β linearly depended on the distance.

Figure 5 shows the time stability of the field emission current density. The maximum fluctuation of the field emission current density is within ± 69.3 μA/cm^2. The standard deviation of the field emission current density is about 12.7 μA/cm^{2}and the standard deviation ratio is 1.79 %. These data show that the field emission current density of the SiNW array fabricated by using the chemical etching method has a high stability when the average field emission current density is about 709.0 μA/cm^2.

IV. CONCLUSIONS

The microstructure and the thickness of a silver catalyst film highly affect the morphology of a SiNW array during the chemical etching processing. The turn-on field of SiNW arrays is about 4.2 V/μm and is lower than other reports. The field enhancement factor β of the SiNW arrays can reach 1637. The SiNW array has a higher time stability during the electron field emission at a current density at 709.0 μA/cm^2. These data indicate that vertically aligned silicon nanowire arrays with uniform structures and high electron field emission have been synthesized by using a chemical etching process with a magnetron sputtering method.

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