



Synthesis and Optical Characterization of Silicon Nanowires via Metal-Simulated Chemical Etching

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Abstract

This paper presents the findings of a comprehensive study on the characteristics, creation, and optical properties of silicon nanowires (SN) formed through metal-stimulated chemical etching (MSCE) of single-crystal silicon, considering both hole and electronic types of conductivity. Our investigation aims to deepen the understanding of key factors contributing to SN genesis. Notably, a direct correlation has been established between the duration of chemical etching and the resultant silicon nanowire's (SN) length, irrespective of the total etching time. The research encompasses an exploration of various spectral phenomena, including total and specular infrared (IR) reflection, Raman scattering (RS) of light generated by WHs, photoluminescence (PL) spectra, and more. Remarkably, the study reveals a noteworthy linear relationship between the duration of chemical etching and the length of the silicon nanowires. Furthermore, our investigation into diverse spectral phenomena, such as total and specular infrared (IR) reflection, Raman scattering (RS) from light generated by WHs, and photoluminescence (PL) spectra, elucidates intriguing patterns. Specifically, the silicon band in the Raman spectrum demonstrates an increase in size and a migration towards shorter wavelengths with prolonged chemical etching time.

1. Introduction

Recently, there has been a growing interest in Crystalline Nanowires (CNs) obtained via the Metal-Assisted Chemical Etching (MACE) method [1–3]. These CNs exhibit physicochemical properties distinct from bulk crystalline silicon. Increasingly, research is being conducted on the application of Quantum Wells (QWs) in fields such as nanoelectronics [4], optoelectronics [5], biomedicine [6], as materials for Giant Raman Spectroscopy (GRS) [7], and as anode materials for lithium-ion power sources [8, 9].

The MACE method has two variants [10]. The first (single-stage) involves selective chemical etching of silicon in a solution containing metal ions and hydrofluoric acid (HF), where metal particles are deposited on the silicon surface while simultaneously etching the silicon to form CNs. The second variant (two-stage) initially forms metal nanoparticles on the silicon surface, followed by chemical etching in a solution containing HF and hydrogen peroxide (H₂O₂). This method allows for more precise control over the structural parameters of the

formed CNs. This paper presents the results of forming CN arrays using the two-stage MACE method on both p-type and n-type single-crystal silicon substrates. It also discusses the optical properties of the resultant CNs.

2. Experimental Procedure

The initial substrates were p-type single-crystal silicon wafers, doped with boron, and antimony-doped n-type silicon wafers. Both had a (100) crystallographic surface orientation, with resistivities of 12 ohm.cm and 0.01 ohm.cm, respectively. We cut 1×1 cm samples from these wafers. The samples were cleansed of organic impurities in a saturated solution of CrO_3 in H_2SO_4 (conc.) and the natural oxide was removed using a 4.5% aqueous HF solution. Silver deposition was performed via immersion in a water-alcohol solution containing 10 mM AgNO_3 and 2.5 M HF for 3 minutes. All experiments were conducted at room temperature.

For selective chemical etching, we used an aqueous solution of 5 M HF and 0.3 M H_2O_2 . Single-crystal silicon wafers with silver nanoparticles were immersed in this solution for varying durations, from 1 to 60 minutes. After etching, the samples were rinsed in distilled water and ethanol and then air-dried. The surface and chips of the samples at different preparation stages were examined using a Hitachi-S4800 scanning electron microscope.

3. Results and Discussion

When a silicon wafer is immersed in a water-alcohol solution of AgNO_3 and HF, Ag ions capture electrons from the silicon's near-surface region, reducing to atomic form and depositing on the wafer surface. Concurrently, silicon oxidation occurs around the Ag nanoparticles.

Figure (1) presents SEM images of the surface and cleavage of a p-type silicon sample after silver particle deposition. As seen in Figure (1), Ag nanoparticles are spaced 10 to 150 nm apart, ranging in size from 50 to 200 nm. Silver dendrites up to $2 \mu\text{m}$ in height are also observed. The silicon surface under the Ag nanoparticles is partially oxidized and etched by HF, creating cavities varying from 20 to 100 nm in size.

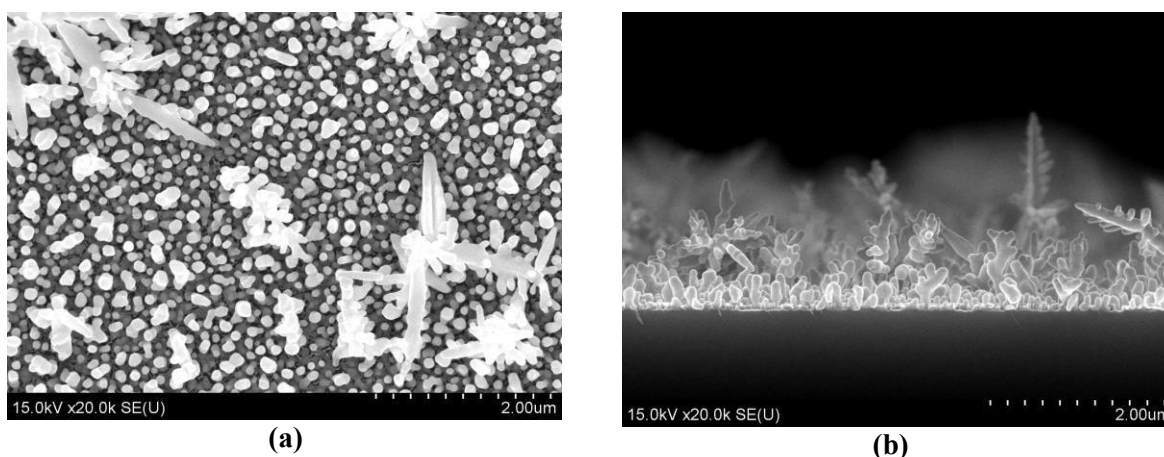


Figure (1): SEM images of (a) surface and (b) cleavage of Si/Ag structures.

Figure (2) shows SEM images of CN arrays formed in an aqueous solution containing 5 M HF and 0.3 M H_2O_2 for 60 minutes on p-type and n-type wafers.

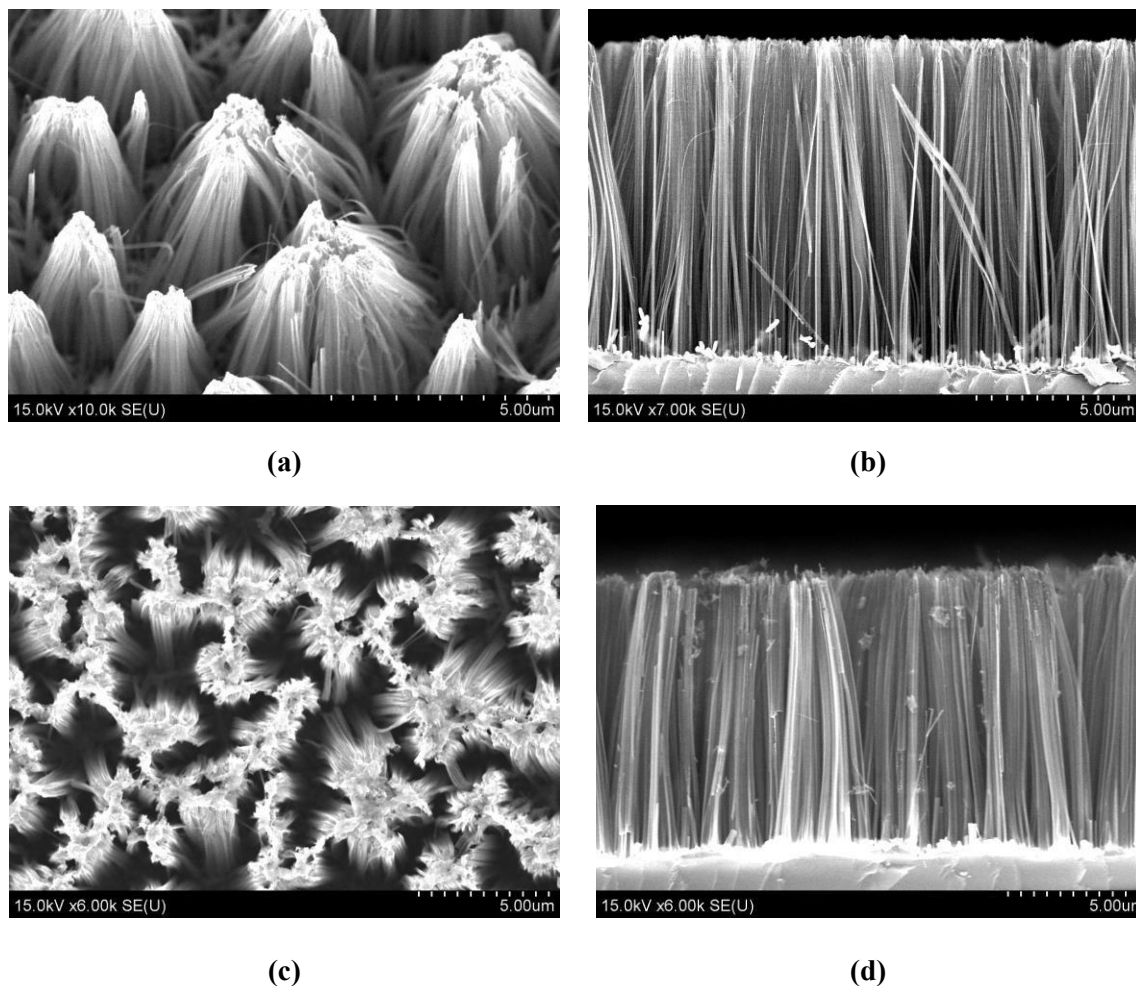


Figure (2): SEM images of the surface (a, c) and cleavages (b, d) of CN arrays obtained by MACE after 60 minutes of etching single-crystal silicon.

In the solution oxide forms under the silver nanoparticles, which then etch away, allowing the particles to embed vertically into the substrate. These results in CN arrays with lengths of 10 and 8 μm for p-type and n-type silicon samples, respectively (Figure 2 b, d). The diameters of these CNs range from 30 to 150 nm. Figure (3) illustrates the dependence of CN length on chemical etching time for silicon wafers of different conductivity types.

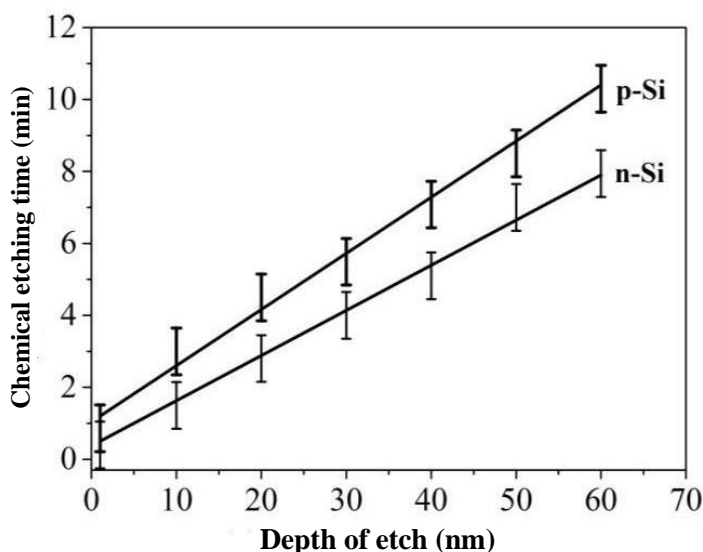


Figure (3): Dependence of CN length on etching time.

As observed in Figure (3), the length of CNs on both p-type and n-type single-crystal silicon substrates increases almost linearly with chemical etching time. The formation rate of CNs varies between the two substrate types 158 nm/min for p-type silicon and 125 nm / min for n-type silicon. Figure (4) presents specular Infrared (IR) reflection spectra, while Figure (5) displays total (diffuse and specular) reflection spectra in the Ultraviolet (UV), visible, and IR ranges for CN arrays on both substrate types.

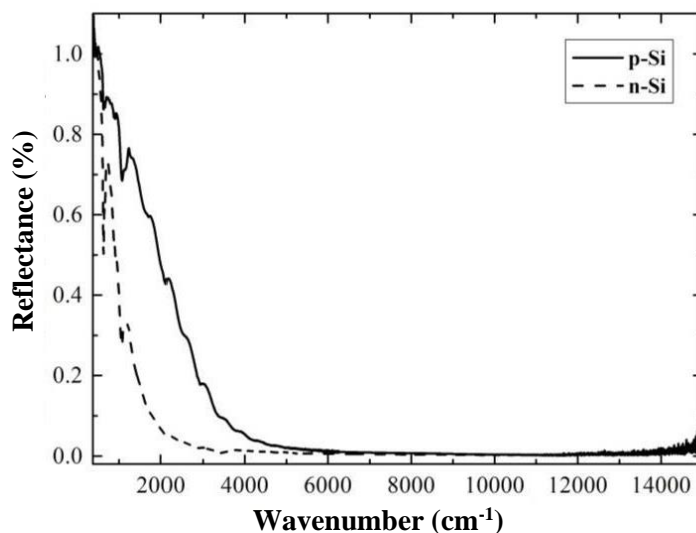


Figure (4): Specular IR reflection spectra of CN arrays.

As can be seen from Figure (4), KN reflects light very weakly in the region of 6000–14000 cm^{-1} , which indicates strong scattering and absorption of light.

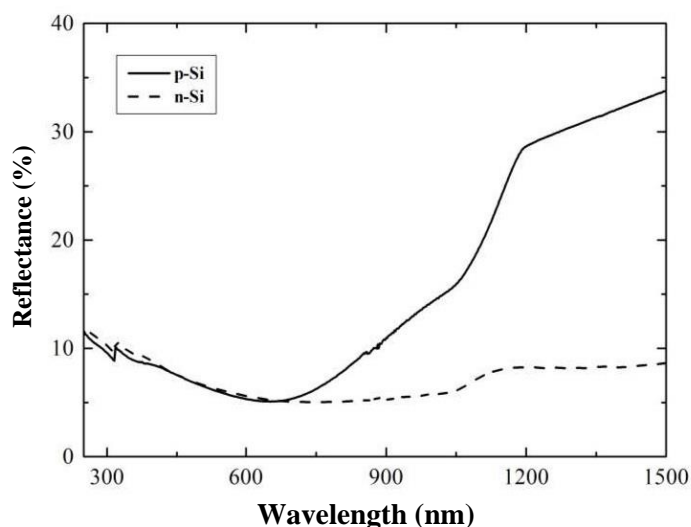


Figure (5): Total reflection spectra in the visible and near-IR ranges for CN arrays.

As evident from Figure (4), CNs weakly reflect light in the $6000\text{--}14000\text{ cm}^{-1}$ range, indicating significant light scattering and absorption. Figure (5) demonstrates that in the visible spectrum, total reflection from CNs is below 10%. In the near-IR range, the total reflection coefficient increases. For CN arrays formed by the MACE method, both Photoluminescence (PL) and Raman spectra were analyzed. PL was excited using 1064 nm radiation, allowing observation of interband PL and Raman signals.

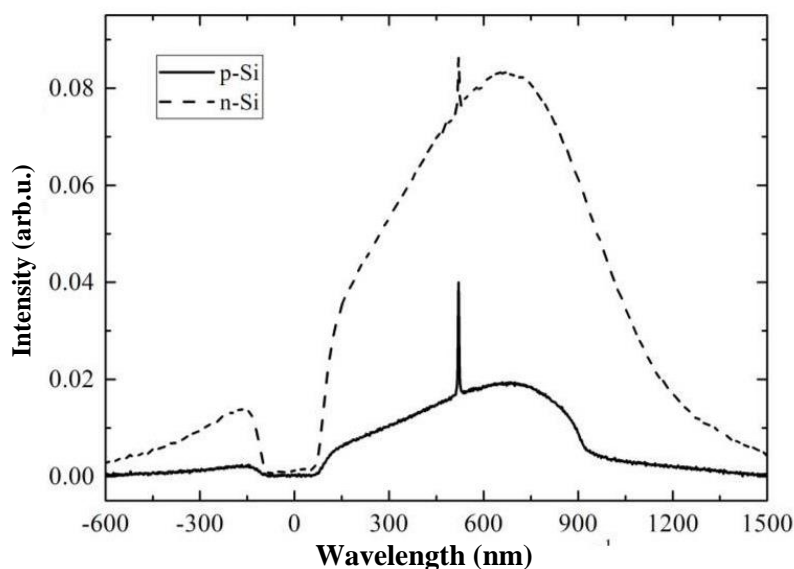


Figure (6): PL and Raman spectra of CN arrays. The spectra were recorded with a notch filter to suppress the excitation line.

CN arrays on n-type silicon substrates show higher interband PL intensity. Figure (7) presents Raman spectra of CNs formed by the MACE method over various etching durations. The spectra were measured using a 473 nm laser. As shown in Figure (7), CNs formed within 1 minute display a marked increase in Raman signal intensity compared to the single-crystal silicon substrate. This could be due to the short length of the CNs and the proximity of silver nanoparticles to the measurement region, contributing significantly to Raman signal enhancement.

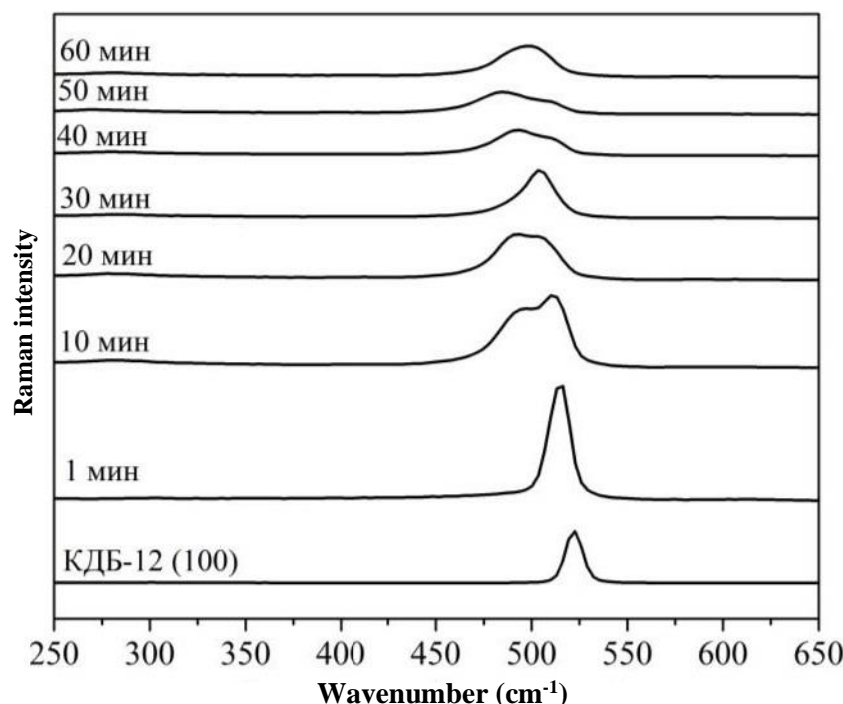


Figure (7): Raman spectra of CN arrays over different etching durations.

The shift towards shorter wavelengths and broadening of the silicon band in the Raman spectrum with increasing etching time may be attributed to the growth of silicon nanocrystallites on the CN surface. These nanocrystallites are known to contribute to the visible PL of QWs [2]. The low-frequency bifurcation of the Raman lines from the CNs could result from heating under the absorbed radiation, even at low intensity.

4. Conclusions

Using the MACE method, CN arrays with lengths of 10 and 8 μm were successfully formed on p-type and n-type single-crystal silicon substrates, respectively. The thickness of the CNs linearly depends on the chemical etching time. Both specular and total reflection spectra were studied, revealing that the formed CN arrays exhibit low specular reflection coefficients due to strong light scattering and absorption. CN arrays on n-type silicon substrates demonstrate a high intensity of interband PL.

Conflict of Interest: The authors declare that there are no conflicts of interest associated with this research project. We have no financial or personal relationships that could potentially bias our work or influence the interpretation of the results.

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