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Synthesis, Properties and Applications of Silicon Nanowire Materials

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Abstract:

This study mainly discusses the preparation, properties, applications and potential issues of silicon nanowires(SiNWs). In terms of preparation, the vapor-liquid-solid growth mechanism is adopted, with gold and zinc selected as catalysts, silane as the silicon source, and chemical vapor deposition method used to prepare gold-core and zinc-core silicon nanowires. In the thermoelectric field, SiNWs have a ZT value far exceeding that of ordinary silicon materials, which can significantly reduce thermal conductivity without affecting electrical conductivity. They are suitable for chip waste heat recovery and micro power generation equipment. As a negative electrode material for lithium-ion batteries, SiNWs have high Coulombic efficiency, high energy capacity, long cycle life, and excellent electrical conductivity, making them excellent materials for the negative electrode of lithium-ion batteries. In the field of electronic devices, by controlling the boron doping and phosphorus doping of silicon nanowires, they can exhibit the characteristics of p-type and n-type semiconductors, while the ohmic properties are improved. In addition, highly doped SiNWs have an extremely small Coulomb blockade effect. Therefore, SiNWs can be applied in field-effect transistors (FETs), p-n junctions, and sensors. Meanwhile, their exceptional light-traking ability, outstanding anti-reflection properties, radial p–n junction structure, tunable surface roughness, and high short-circuit current density enable promising applications in solar cells. Despite their promising application potential, the currently high manufacturing costs of SiNWs hinder large-scale adoption, indicating a need for further research in this area.

Keywords: Silicon nanowires; vapor–liquid–solid; chemical vapor deposition; Application.

1. Introduction

Compared with bulk silicon materials, silicon nanowires(SiNWs) possess numerous advantages due to their nanoscale size, thus enabling their applications in various technological fields. In the field of thermoelectric, the dimensionless figure of merit (ZT) of silicon nanowires is significantly higher than that of crystalline silicon. SiNWs can drastically reduce thermal conductivity while barely affecting electrical conductivity. Consequently, such SiNWs thermoelectric materials hold promising application prospects in areas including chip waste heat recovery, precise cooling of electronic devices, and micro-power generation equipment[1].

In the field of batteries, the initial charge capacity of SiNWs is basically consistent with the theoretical capacity of $Li_{4.4}Si$, which is significantly higher than previous results[2,3]. The Coulombic efficiency during discharge is quite high. During subsequent cycling processes, the charge-discharge capacity remains essentially stable without obvious degradation within 10 cycles. Even under high-rate conditions, SiNWs can still maintain a relatively high capacity output. Moreover, the discharge capacity remains stable at different discharge rates. During the charging process, although both the length and diameter of SiNWs increase, the nanowires always remain continuous without fracture and maintain good contact with the substrate . The current-voltage (I-V) curve of pristine silicon nanowires shows a linear relationship. After one charge-discharge cycle, the I-V curve still maintains linearity; although the resistance increases slightly, the nanowires still possess good electrical conductivity. Therefore, the application of SiNWs as anode materials in lithium-ion batteries can significantly enhance the energy capacity and cycle life of the batteries[4]. In addition, owing to their tunable doping profiles, high structural and electronic uniformity, adjustable conductivity, favorable ohmic contact behavior, and inherent benefits of one-dimensional nanostructures, SiNWs are well-suited for use in electronic devices [5]. Furthermore, their remarkable light-harvesting capacity, excellent anti-reflection characteristics, radial p–n junction configuration, controllable surface roughness, and high short-circuit current density render them highly attractive for solar cell applications[6]. This paper mainly discusses the preparation methods and growth mechanisms of SiNWs using gold and zinc as nucleation catalysts, respectively. It also summarizes the excellent properties and application potential of SiNWs, and addresses the limitations in their practical applications.

2. Preparation Methods of SiNWs

SiNWs were synthesized via the vapor–liquid–solid (VLS) mechanism[7,8] at temperatures between 450–500°C, using either gold or zinc as the catalyst and silane as the silicon source. The resulting Au–SiNWs and Zn–SiNWs exhibited an average diameter of approximately 20 nm[9].

2.1 Preparation of Gold-Core Silicon Nanowires (Au-SiNWs)

Silane was deposited on gold-plated silicon wafers via the CVD method. Using the electron beam evaporation technique, a gold film with a thickness of 0.5–1 nm was formed on the surface of a silicon dioxide substrate coated with a 150 nm-thick layer, resulting in the formation of a gold island structure[10]. The product from the previous step was heated isothermally at 400–450°C under a pressure of 10^{-3} Torr for one hour. Subsequently, the temperature of the reaction furnace was adjusted to 450°C, and He containing 5% SiH_4 was introduced at a flow rate of 300 SCCM under a constant pressure of 100 Torr, with the process lasting for 20–40 minutes[9].

2.2 Preparation of Zinc-Core Silicon Nanowires (Zn-SiNWs)

A p-type boron-doped Si(100) wafer was selected, and an aluminum film serving as the anode was coated on its backside. The wafer was then placed in an electrolytic cell for etching, with a platinum electrode used as the cathode. A mixture of hydrofluoric acid and absolute ethanol at a volume ratio of 2:3 was employed as the electrolyte, and the reaction was conducted under a constant current density of 10 mA/cm² for 3–5 minutes, ultimately forming a porous silicon layer with an average pore size of 1–3 nm. Subsequently, the aforementioned product was immersed in a zinc chloride/ethanol solution for ultrasonic cleaning, which lasted for 30–60 minutes. The cleaned product was rinsed multiple times sequentially with 2-propanol and 18 MΩ·cm water, followed by drying with flowing nitrogen. Next, annealing was performed for 3 hours in a quartz tube under a vacuum of 10^{-3} Torr at 450°C. While maintaining this temperature, a 5% H_2/Ar mixed gas was continuously introduced for purging over 5 minutes, after which a silane/helium gas flow treatment was carried out. Finally, Zn–SiNWs (zinc-silicon nanowires) were grown at 450–500°C for 30–60 minutes under a total pressure of 50–100 Torr, using 5% silane/helium gas with a flow rate of 300 SCCM[9].

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3. Application of Silicon Nanowires

3.1 Thermoelectric

By adjusting the dimensional parameters of nanowires and the impurity doping concentration, the ZT value of silicon nanowires has been increased by nearly 100 times compared with that of bulk silicon over a wide temperature range. Specifically, a ZT value of approximately 1 can be achieved at 200 K, significantly surpassing that of bulk silicon (ZT ≈ 0.01 at 300 K). This remarkable improvement stems primarily from a substantial reduction in thermal conductivity (κ) due to phonon boundary scattering and one-dimensional quantum confinement, without significantly compromising electrical conductivity (σ). Moreover, as phonon transport transitions from a three-dimensional to a one-dimensional regime, and boundary restrictions on the phonon mean free path are relaxed, the phonon drag effect re-emerges. This leads to a considerable enhancement in the Seebeck coefficient (S), thereby contributing to the overall increase in the ZT value. Owing to these advantageous characteristics, SiNWs-based thermoelectric materials demonstrate promising potential for applications such as on-chip waste heat recovery, precision cooling of electronic devices, and micro-scale power generation[1].

3.2 Anodes of Lithium-Ion Batteries

From an electrochemical performance perspective, SiNWs exhibit a first charge capacity of 4277 mAh/g during charging and discharging, which aligns well with the theoretical capacity of $Li_{4.4}Si$. During discharge, a relatively high Coulombic efficiency is maintained. More importantly, the charge and discharge capacities remain largely stable over subsequent cycles, with no significant decay observed within 10 cycles—a performance markedly superior to other anode materials. Even under high current rates, SiNWs maintain a high capacity output. At various rates, their discharge curves display stable voltage plateaus, and their capacities far exceed those of graphite anodes. These results demonstrate the excellent rate capability and cycling stability of SiNWs. From a structural evolution standpoint, significant volume expansion occurs upon lithiation, yet the structural integrity is preserved without detachment from the current collector. This effectively mitigates capacity fading caused by loss of electrical contact. In the nickel evaporation experiment, it was observed that after the lithiation of SiNWs, a three-dimensional spiral structure was formed around the nickel framework. This phenomenon proves that the length of the SiNWs also increased, but there was still no structural fracture; therefore, electrons still have a very good transmission path. By comparing the changes in the current-voltage (I-V) curves of a single silicon nanowire before and after lithiation, it was found that the I-V curve of the original SiNWs was linear. After one charge-discharge cycle, the I-V curve remained linear, but both the resistance and resistivity increased. However, even the lithiated SiNWs still exhibited excellent electrical conductivity, which demonstrates that SiNWs possess efficient electron transport capabilities during the charge-discharge process. Owing to these properties, SiNWs are excellent materials for use as anodes in lithium-ion batteries, significantly enhancing their energy capacity and cycle life[4].

3.3 Electronic devices

During the preparation of SiNWs, boron doping or phosphorus doping can make SiNWs exhibit p-type or n-type semiconductor characteristics. Compared with undoped SiNWs, the I-V curve of boron-doped SiNWs is linear, so they possess ohmic properties. When the gate voltage changes, the conductivity changes in the opposite direction. Moreover, the resistivity of boron-doped SiNWs is significantly lower than that of undoped SiNWs, thus giving them better electrical conductivity. Meanwhile, as the boron doping concentration increases, the resistivity decreases further. The conductivity of boron-doped silicon nanowires decreases with the decrease in temperature, and the Coulomb blockade effect is very weak. For phosphorus-doped SiNWs, the variation trend of conductivity with gate voltage shows the same direction. As the doping concentration increases, the linearity of the I-V curve improves, thereby enhancing the ohmic properties. Owing to these properties, SiNWs can be applied in field-effect transistors (FETs), p-n junctions, and sensors [5].

3.4 Solar Cells

SiNWs possess superior light scattering, carrier trapping capabilities, and coupling performance. By optimizing the preparation process of SiNWs, the fill factor, voltage output, and current density can be significantly improved. By adjusting the roughness factor, SiNWs can achieve high conversion efficiency. The presence of SiNWs significantly reduces the intensity of transmitted light, indicating their excellent light-trapping effect. Increasing the length of SiNWs can enhance the recombination efficiency and light absorption capacity. Most importantly, after appropriate modification of the geometric structure on the surface of SiNWs, they can tolerate a lower roughness factor level with almost no impact on the light-trapping effect. Owing to these properties, SiNWs hold extremely high value and advantages in the field of high-efficiency thin-film solar cells[6].

4. Opportunities and Challenges

Owing to the relatively high cost of SiNWs, challenges persist in their large-scale applications. Taking Amprius Corporation as an example, the lithium-ion batteries fabricated using SiNWs by this company exhibit remarkably excellent performance, even outperforming Tesla's batteries. However, their application in electric vehicle batteries is not feasible, primarily due to excessively high costs. Therefore, future research should focus on exploring effective strategies to reduce costs without compromising the performance of SiNWs.

5. Conclusion

This study elaborates on the synthesis methodology, growth mechanism, advantages, and applications of SiNWs. The SiNWs were synthesized on solid substrates via the VLS growth mechanism, using gold or zinc as the catalyst and silane as the silicon source. Two types of nanostructures were produced: Au–SiNWs and Zn–SiNWs. Both types were fabricated as bulk materials within the aforementioned temperature range by CVD.

SiNWs possess several notable advantages. In the field of thermoelectrics, their low-dimensional structure significantly reduces κ while markedly enhancing S, making them promising candidates for thermoelectric materials. In battery applications, SiNWs demonstrate a first-charge capacity consistent with the theoretical capacity of $Li_{4.4}Si$, high Coulombic efficiency upon discharge, excellent cycling stability, and the ability to accommodate volume expansion without fracture, all while maintaining good electrical conductivity. These properties render SiNWs-based materials highly suitable for use as anodes in lithium-ion batteries. The combination of controllable doping, high structural and electronic homogeneity, broadly adjustable conductivity, low-resistance ohmic contacts, and unique one-dimensional confinement effects makes SiNWs highly suitable for electronic devices. On the other hand, their superior light-trapping performance, excellent anti-reflection properties, radially configured p–n junctions, engineerable surface morphology, and high short-circuit current densities under recombination losses offer significant advantages for solar cell applications. However, the relatively high cost of SiNW remains an issue that requires further resolution in subsequent studies.

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