Preparation method and application of silicon nanowires

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Abstract. In recent years, silicon nanowires have become a hot spot in the new material industry. As a kind of nanomaterial, silicon nanowires have excellent physical and chemical properties. However, the preparation method of silicon nanowires is not mature enough, which limits its further application. This paper mainly analyses the mechanism, advantages and disadvantages of several mainstream silicon nanowires preparation methods, and discusses the application of silicon nanowires and the future development direction. The results show that the chemical vapor deposition method can be used for large-scale preparation of silicon nanowires, while the laser ablation method can produce silicon nanowires with higher purity, and the electron beam lithography method has the advantages of high flexibility. However, the efficiency of these three methods is not high, and the cost is high, which is also the problem that the silicon nanowire preparation industry is looking forward to solve. Relying on the excellent conductivity, thermal conductivity and other characteristics of silicon nanowires, silicon nanowires can be applied to a variety of new energy industries. Based on the properties of silicon nanowires, this paper analyses the application of silicon nanowires in lithium batteries, solar cells, biosensors and thermoelectric materials in recent years, and forecasts its development trend, so as to provide a certain reference for researchers to further explore the research of silicon nanowires.

Keywords: Silicon nanowire, Chemical vapor deposition, Laser ablation, New energy.

1. Introduction

Silicon nanowires (SiNWs) are a typical representative of one-dimensional nanomaterials. In addition to the unique characteristics of silicon as a semiconductor, silicon nanowires also exhibit characteristics distinct from bulk silicon materials, such as field emission, thermal conductivity, and visible light luminescence. It has great potential application value in nano electronic devices, photoelectronic devices and new energy sources. More importantly, silicon nanowires are highly compatible with existing silicon technologies and thus has great market potential. Therefore, silicon nanowires are a type of new material with great potential in the field of one-dimensional nanomaterials. However, at present, the preparation method of silicon nanowires is still immature, and there are certain defects in equipment requirements, preparation scale, production cost and product purity. At the same time, due to some physical effects of nanomaterials themselves, silicon nanowires also have various problems in practical application, which limits the development of new energy and other industries to a certain extent.

At present, there are many preparation technologies for silicon nanowires, which can be divided into two types according to their growth patterns, namely, "top-down" and "bottom-up" technologies. "Bottom-up" is the pattern of growing nanostructures from the atomic level through continuous deposition in the form of self-assembly. It mainly includes chemical vapor deposition, molecular beam epitaxy, laser ablation, oxide assisted method and solution method. The "top down" process starts with etching the template, carving the sample into a growth pattern of nanostructures of the desired size. The methods include electron beam lithography (EBL), nanoimprint lithography and metal-assisted chemical etching. Based on these two growth modes, Hu et al [3]. summarized the preparation methods of silicon nanowires. However, for the specific application of silicon nanowires and analysis of the application, there are few related summary articles. Therefore, on the basis of studying the preparation methods of silicon nanowires, this paper summarizes and analyses several applications of silicon nanowires.

In this paper, three main fabrication methods of silicon nanowires, chemical vapor deposition, laser ablation and electron beam lithography, are discussed. Based on the mechanism of these three methods, this paper introduces their respective advantages and analyses their defects according to the actual industrial production. In addition, several applications of silicon nanowires in the field of new energy and biomedicine are also introduced, including lithium batteries, solar cells, biosensors and thermoelectric materials. Finally, this paper analysed the advantages and disadvantages of silicon nanowires in the application of these products, and prospected its development trend, so as to provide a certain reference for researchers to further explore the research of silicon nanowires.

2. Silicon nanowires

2.1. Silicon nanowires

Nanowire is a one-dimensional material that is limited to less than 100 nanometers laterally and has no limit longitudinally. Nanowires are also called "quantum wires" because at this scale, quantum mechanical effects are apparent. Nanowires can be classified into a variety of varieties depending on the composition of the various materials used, including metal nanowires (such as Ni, Au, Pt, etc.), semiconductor nanowires (such as Si), and insulator nanowires (such as SiO_2, TiO_2). The repeating molecules that make up molecular nanowires can be either organic (like DNA) or inorganic (such as MO_6S_9-XIX) [1].

Among them, silicon nanowire is a brand-new type of one-dimensional semiconductor nanomaterial with a diameter of typically around 10 nm. Its outer layer is covered with SiO_2, and its inner crystal core is monocrystalline silicon. Due to their unique optical and electrical properties, such as quantum confinement effect and Coulomb blocking effect, silicon nanowires have attracted extensive attention in the field of science and technology. At present, the application of silicon nanowires in battery and sensor fields has made some progress.

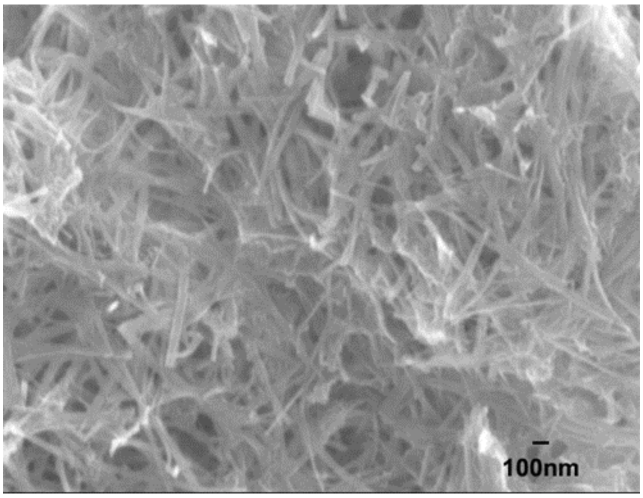

Figure 1. Microstructure of silicon nanowires [2].

Figure 1 shows the microstructure of silicon nanowires. It is about 10nm in diameter and about 200nm in length. This one-dimensional nanostructure makes silicon nanowires possess excellent physical and chemical properties. However, limited by the preparation scale of silicon nanowires, the current price of silicon nanowires is extremely high, with about $1038 per gram [2].

2.2. Preparation methods of silicon nanowires

2.2.1 Chemical Vapor Deposition (CVD).

Nowadays, CVD is a relatively common method to prepare silicon nanowires. The principle is shown in the following Figure 2.

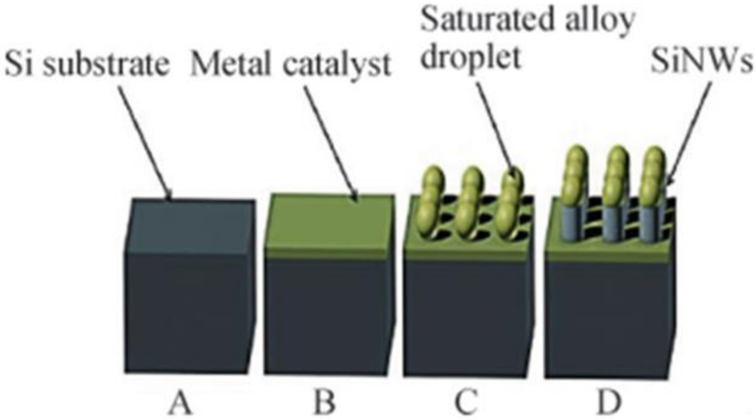

Figure 2. Growth of silicon nanowires by CVD [3].

There are mainly six steps in this process. First, gaseous silicon starts to diffuse in the system. Secondly, a metal film of a few nanometers is plated on the surface of the substrate as a catalyst. After that, the silicon gases are adsorbed by the substrate surface, which leads to the chemical reaction occurring on the substrate. Finally, silicon nanowires are deposited in the substrate to nucleate for regrowth, followed by the desorption, dispersion and volatilization of gases [3]. The growth of silicon nanowires by this method is actually a gas-liquid-solid three-phase process, namely the vapour-liquid-solid mechanism (VLS). The vapour-liquid-solid mechanism was originally proposed by Wagner and Ellis [4], who pointed out the importance of metal catalysts in the growth process of silicon nanowires, which is the most common method to prepare silicon nanowires. It is also the most effective method to realize the industrial production of silicon nanowires. At present, the primary advantage of CVD method is that it can be used for macrofabrication of silicon nanowires. Besides, the reaction time is short, ranging from 10 to 30 min, and the equipment operation is simple. However, the deposition rate of CVD is low and the equipment used in CVD method is expensive, which limits the further application of the CVD method.

2.2.2 Laser Ablation (LA).

Figure 3 shows the schematic diagram of silicon nanowires prepared by LA. This technique is also known as laser evaporation technology. This method is still essentially based on VLS as the growth mechanism. The principle is to use laser as a heat source to heat the target containing metal powder, thereby *evaporating* a large number of target atoms, which are rapidly condensed in an inert gas (Ar or N_2) atmosphere, and finally form silicon nanowires on the substrate [5]. Lieber et al. [6] first proposed the laser ablation technology combined with the growth mechanism of metal VLS, and could easily prepare a large number of silicon nanowires with a diameter of about 10 nm.

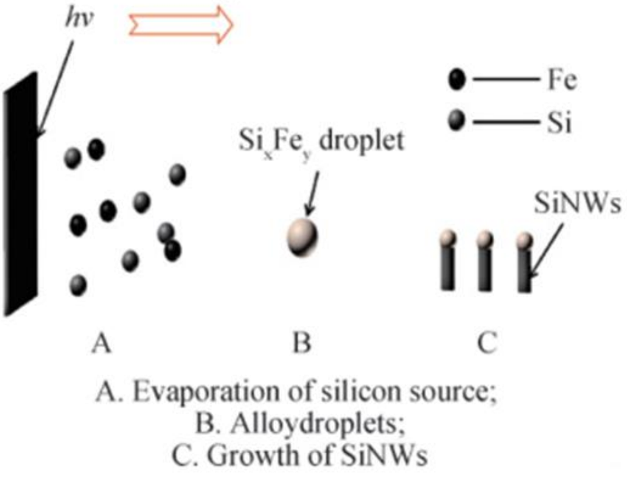

Figure 3. Preparation of silicon nanowires by LA [5].

Compared with CVD metal film catalyst, laser ablation requires the catalyst and elemental silicon source to be fused into a whole. In addition, when growing silicon nanowires, part of the product grows in the gas phase. At present, in the preparation of silicon nanowires by LA method, the phase diagram is usually analyzed in order to select the appropriate amount of catalyst and the temperature required for the reaction. The resulting silicon nanowires are less than 20 nanometers in diameter, which is typically smaller than those made by other methods. This also makes LA method has the advantages of high purity, easy operation, good controllability and so on. However, the disadvantages of this method are high equipment requirements and slow growth rate [3, 6].

2.2.3 Electron Beam Lithography (EBL).

Figure 4 shows *the* growth of silicon nanowires by electron beam lithography [7]. It means that the silicon substrate is etched to form electron beam mark, the photoresist (PR) is removed, the glue is spun, the hard mask pattern of the nanowire is obtained by electron beam lithography, the silicon substrate is etched, the photoresist is removed, and finally the silicon nanowire is obtained. Different from the "bottom-up" principle of the above two technologies, EBL, as a "top-down" method, starts with etching pretreatment of the template, that is, carving the sample into a growth pattern of nanostructures of the desired size. The technology has extremely high resolution, up to nanometer level, and the smallest fabrication size is 10 ~ 20 nm. Because E-beam lithography is maskless, it is highly flexible and can be used to directly produce different types of graphics, but yields are extremely low. In addition, the *etching* depth is difficult to control accurately. The complex equipment structure also leads to the high cost of this method.

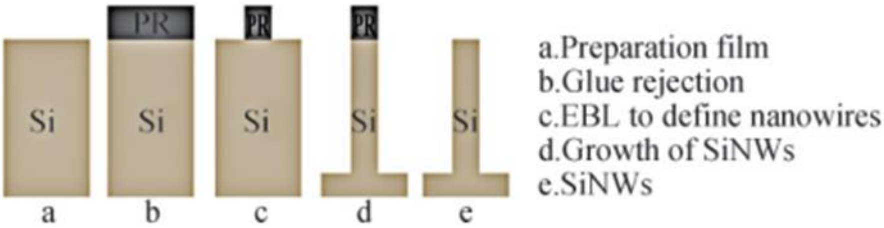

Figure 4. Growth of silicon nanowires by EBL [7].

3. Application of silicon nanowires

3.1. Lithium battery

The current commercial anode material graphite has a relatively low theoretical capacity (372 mAh/g), which is difficult to meet the increasing energy demand. As can be seen in Figure 5, silicon is environmentally friendly, rich in resources, low potential of lithium inlays, and working voltage close to graphite. Besides, the theoretical specific capacity (4200 mAh/g, $Li_{22}Si_5$) is the highest among the current alloy anode materials, so it is considered as the most promising alternative anode materials [8, 9].

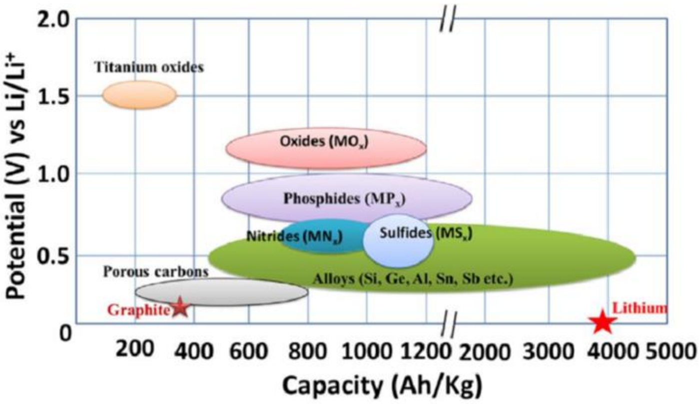

Figure 5. The active anode material of lithium battery [8].

However, silicon materials still suffer from severe volume changes (~300%) during cycling and low electrical conductivity (less than 10-3s /cm at room temperature). Figure 6 illustrates the failure mechanism of silicon in a cell. The stress generated by the severe volume expansion leads to the electrode pulverization and breakage as well as the loss of electrical contact between materials. What's more, volume change also causes the weakening of contact between materials and collectors and the formation of unstable SEI film, resulting in rapid capacity decay [10].

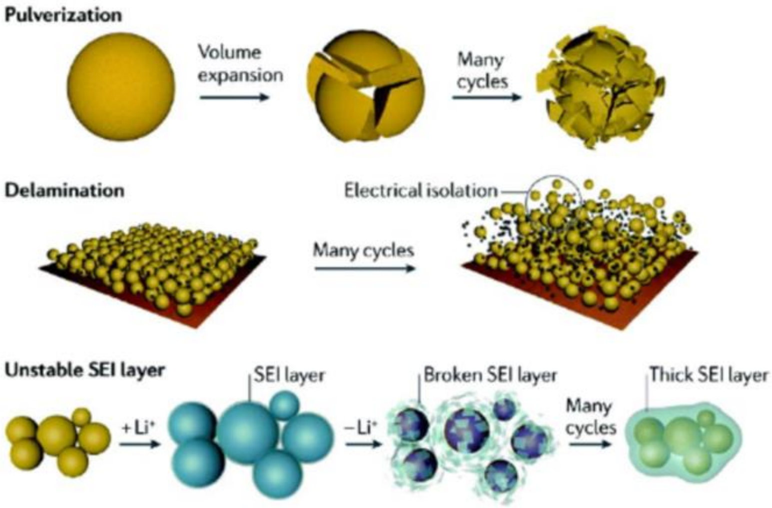

Figure 6. Failure mechanism of silicon cells [8].

As a solution to this problem, nano-silicon material can shorten the diffusion distance of lithium ion in the anode material and improve the electrochemical reaction rate. Silicon nanowires can also reduce the change of radial volume during the cycle so that the battery can obtain good cycle stability. In addition, silicon nanowires can provide fast transport channels for lithium ions in their axial direction. Based on these advantages, silicon nanowires have broad application prospects in the battery field. In recent years, Amprius [11] has introduced a series of new silicon nanowire lithium-ion batteries, and is working to apply them to electric vehicles and aviation.

3.2. Solar energy cell

Silicon nanowire solar cells work like other solar cells through three important processes: photon absorption, charge separation, and charge harvesting. Firstly, the silicon nanowires are doped to form P-type and N-type semiconductors, and the contact area of the two forms PN junction, and then the electric field is formed inside. Finally, the photogenerated electric field is generated under sunlight irradiation, and the current is generated when the external load is connected. In this process, the most important is the formation of the built-in electric field and the photogenerated electric field [12].

Compared with planar crystalline silicon solar cells, silicon nanowire solar cells can enhance the absorption of light. Studies have shown that the absorption capacity of silicon nanowires to light is 73 times that of planar silicon of the same thickness [13]. At the same time, theoretical calculation proved that the same absorption rate, silicon nanowires can save 91% of silicon materials [14, 15].

Silicon nanowire solar cells have advantages and potential in the silicon-based solar cell market due to their low cost and easy availability of raw materials. But silicon nanowire solar cells are not yet commercially available. The main problem is the low conversion efficiency of silicon nanowire solar cells. There are also many issues and challenges that need to be addressed. For example, crystal defects on the surface of silicon nanowire lead to heterogeneous properties such as chemical stability of the cell, which also limits the further development of silicon nanowire solar cells.

The conversion efficiency of silicon nanowire solar cells is closely related to their extinction ability. At present, it is found that further optimization of the symmetry of silicon nanowires can achieve good extinction of natural light. Gao [16] and other researchers designed a silicon nanowire with a three-leaf top view, which increased the extinction capacity of a single nanowire by 85%. The principle of the design is shown in Figure 7. Compared with cylindrical silicon nanowire arrays, the optical absorption of silicon nanowire arrays with three-leaf top view is improved by 23%, and the conversion efficiency of silicon nanowire solar cells is improved by 14.7% [16].

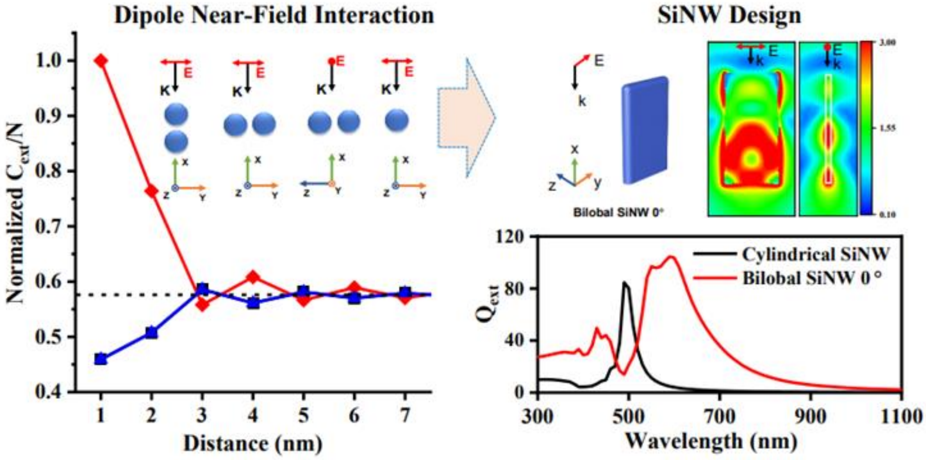

Figure 7. Flow chart of silicon nanowire design principle [16].

3.3. Silicon nanowire field-effect transistor (SiNW-FET) biosensor

SiNW-FET biosensor utilizes the characteristic that the mobility of silicon nanowire carriers is extremely sensitive to charge changes, that is, a small amount of surface charge changes can cause significant changes in conductance, so as to realize ultra-sensitive real-time detection of biomolecules causing different diseases under low concentration conditions, and finally achieve the purpose of early diagnosis of complex diseases [17]. The sensing mechanism of SINW-FET is shown in Figure 8.

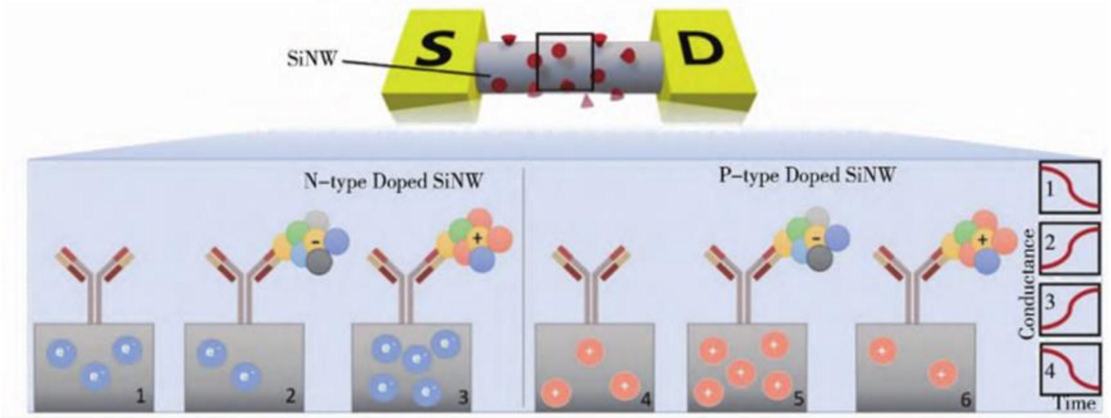

Figure 8. Schematic diagram of sensing mechanism of SiNW-FET [18].

At present, SiNW-FET biosensor has broad application prospects in detecting many important human indicators. In 2001, Cui et al [19]. first used SiNW-FET to explore its response to pH value and calcium concentration changes. In 2017, Anand [20] used SiNW-FET to monitor potassium efflux in cultured cortical neurons in real time. In addition, SiNW-FET can also be used to detect nucleic acid, virus, protein and other important physiological indicators.

However, due to the influence of semiconductor Debye shielding effect, the research of SiNW-FET biosensor directly detecting target molecules in physiological solutions has encountered a bottleneck, and it is difficult to realize the detection of target molecules in high-ionic strength solutions. In addition, the uncharged or weakly charged target molecules have very little effect on the semiconductor channel, which makes it impossible to measure the target effectively. These two aspects greatly limit the clinical application of SiNW-FET biosensor [21]. These problems also provide directions for the subsequent development of SiNW-FET.

3.4. Thermoelectric materials

Thermoelectric materials can directly convert waste heat into electric energy, which is one of the effective ways to alleviate the energy shortage and environmental pollution problems faced by various countries. As the basic element of modern microelectronics and photovoltaic industry, silicon has the characteristics of low price, non-toxic and rich content, and is the pillar of the current high-tech field. However, the traditional bulk silicon materials have high intrinsic lattice thermal conductivity, which greatly limits the wide application of silicon in the thermoelectric field [22]. Due to the small-scale effect, the physical and chemical properties of silicon nanowires are very different from those of bulk materials. Silicon nanowires have excellent electron and phonon transport properties, which makes them have excellent thermoelectric properties. At present, silicon nanowires have the advantages of both silicon and nanostructure, and have broad application prospects in the field of thermoelectric materials.

Researchers at Lawrence Berkeley National Laboratory have developed a new silicon nanowire material [23]. The silicon nanowires have a 150% increase in thermal conductivity compared to traditional natural silicon nanowires and could be used in the field of microchip manufacturing in the future.

4. Conclusion

With its excellent physical and chemical properties, silicon nanowires have great development potential in the field of new energy industry, sensor industry and nanomaterials. Three preparation methods of silicon nanowires are discussed in this paper. The silicon nanowires prepared by CVD method are suitable for industrial mass production, but the deposition rate is low. The purity of silicon nanowire prepared by LA method is higher, but the growth rate of nanowire is lower. EBL method has the advantages of high flexibility, but low yield. In addition, the costs of these three methods are generally higher. In terms of applications, the capacity of lithium batteries is greatly improved by using silicon nanowires as negative electrodes. Also in the battery field, silicon nanowire solar cells have stronger light absorption capacity than traditional solar cells. In the field of biomedicine, biosensors made of silicon nanowires can realize the effect of early diagnosis of complex diseases by virtue of the fact that the mobility of silicon nanowires' carriers is extremely sensitive to charge changes. In addition, silicon nanowires, as high-quality thermoelectric materials, also have wide application prospects in the area of microchips. In the future, researchers should focus on improving the preparation process of silicon nanowires and reducing the production cost, so as to achieve large-scale industrial application of silicon nanowires in the early stage. This paper provides some ideas and suggestions for the future development direction of silicon nanowires, which can provide some references for researchers.

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