Fabrication of Si-Ge Nanowires

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Abstract

Different compositions of Si-Ge nanowires (SGNWs) have been fabricated by Vapor Liquid Solid (VLS) mechanism by using Ni as a catalyst with different $SiCl_4$: $GeCl_4$ ratios and temperatures respectively. The SEM results show that the SGNWs could be grown successfully vertical on the surface of the silicon with temperatures of 1000°C, 950°C, 90°°C and 850°C. But for 900°C and 850°C, some of the NWs were observed to be grown as flower like structures instead of vertical. The growth rates are observed to be depending upon the ratio and the flowing times of the precursors greatly. For equal ratio of precursors ($SiCl_4$: $GeCl_4$=1:1) and the precursors' flowing times of 5 min and 10 min, the growth rates of the SGNWs were observed to be around 20um/min and 30um/min respectively. The SEM results showed that the SGNWs could be grown successfully, vertical on the surface of the silicon with varying temperatures. Keywords: SiGe Nanowire, growth rate, optical characteristics.

Introduction

Currently, one of the most important problems faced by the world is energy supply [1]. Clean energy demand has become strongly important as the increasing consumption of fossil fuels has lead to the global warming and green house gases emissions [2-5]. In this regard Solar energy seems to be the most useful alternate choice to fulfill our clean energy requirement [2]. One dimensional nanostructures particularly nanowires and more specifically Si or Si-Ge Nanowires are supposed to be promising candidates with great potentials to be used for solar cell industry [2]. $Si_{1-x}Ge_x$ axial nanowire (NW) heterostructures have received much attention because of its great potential to be used as promising candidates for electronic, photonic and thermo electronic applications due to significant energy storage and energy generation properties [6]. One of the key issues that determine the efficiency of solar cells is the optical absorption of the wire arrays within the solar spectrum. A relatively weak absorption of Si in the infrared region results the limited achievable conversion efficiency, therefore, taking advantage of lower band gap of Ge as compared to Si, the efficiency can be boosted by alloying Si with Ge which in turn allows absorption to be tuned across a useful range of the solar spectrum [7-8]. Moreover, compared to Si only, $Si_{1-x}Ge_x$ has the ability to capture a wide range of the light spectrum and hence increase the carrier mobility [9].

One of the most attractive techniques to fabricate semiconducting nanowires is the Vapor Liquid Solid method (VLS) [10-13]. Although Gold is most commonly used as catalyst material in VLS, but due to incompatibility of gold with the conventional semiconductor processing technology, Au can form a deep trap level states within the band gap of Si, which will cause serious leakage current governed by Shockley-Read-Hall recombination increasing the rate of carrier recombination when impurities' energy level is located near the Fermi level of Si [14-15]. All of the shortcomings show it is important to alternate catalyst of Au by other elements. We used Ni as catalyst material instead of Au because Ni is cheap, abundant, and Ni has high solubility of Si in the liquid eutectic droplet and low resistivity at the tip of nanowires compared to gold.

In this paper, we use Ni instead of the Au as the catalyst of the VLS methods for the fabrication of the Si-Ge NW with different compositions of Si-Ge nanowires (SGNWs) under different temperatures of 1000°C, 950°C, 900°C and 850°C. Firstly, A 2-nm-thick Ni film was thermally evaporated on the surface of n-Si (111) (1-20 Ω cm) substrate under a base pressure of $5x10^6$ Torr. And then, the SGNWs could be grown successfully vertical on the surface of the silicon by Vapor Liquid Solid (VLS) mechanism by using the formed Ni film as a catalyst under 1000°C in the tube furnace with the precursors' mole ratios of $SiCl_4$: $GeCl_4$ as 2:8, 3:7, 4:6, 5:5, 6:4, 7:3 and 8:2 respectively under different times. We also changed the circumstance temperature of the fabrication from 1000°C to 950°C, 900°C and 850°C respectively. For 900°C and 850°C, some of the NWs were observed to be grown as flower-like structures instead of vertical SGNWs. The optical characteristics of the resulted NWs show great potential in the application of solar cell.

Experimental

A 4 inches n-type (1-20Ωcm) Si (111) wafer was cleaned by immersing it into a blended solution of deionized water and hydrofluoric acid with a mole ratio of 8:1 respectively. Secondly, the wafer was dipped into the D.I water for one minute, and this process was repeated once more in another bottle of

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D.I water. Then the wafer was dried by Nitrogen gas. And then, a 2-nm-thick Ni film was deposited on the surface of the cleaned Si wafer substrate by thermal evaporator under a vacuum pressure of ~$5x10^{-6}$ Torr. Next, the Nickel coated wafer was cut into smaller samples with suitable scale of 1x1 cm^2 by diamond cutter. After ultrasonic cleaning in aceton, the samples were then introduced into a quartz tube in the horizontal tube furnace as shown in Fig. 1 (a), and before the VLS experiments, in the tube furnace Ar gas (10% H_2) was flowed for 30 min at 400˚C so as to remove the oxygen molecules remaining inside the tube. Above eutectic temperature, Ni films could form the nanosized NiSix agglomerates by alloying with Si substrates. These nanosize alloys could act as the metallic catalyst for the vapor-liquid-solid nanowire growth with the precursors. Vertically aligned SGNWs arrays could be grown in the quartz tube furnace by atmospheric

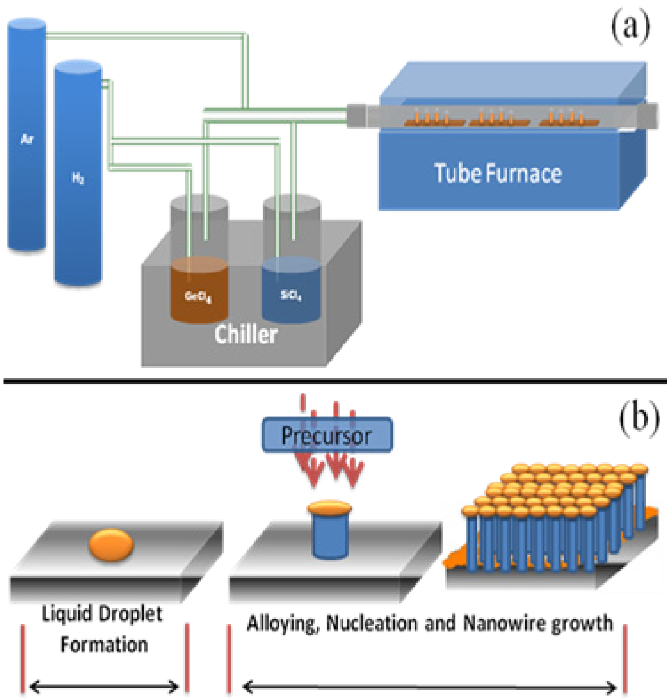

Fig. 1: The schematics of the experimental setup for the SGNWs' growth. (b) The schematics of the dynamical process for the SGNWs' growth.

Pressure, chemical vapor deposition using $SiCl_4$ and $GeCl_4$ as precursors under 1000˚C. The concrete dynamical process is depicted in Fig. 1 (b).

Results and discussion

The concrete fabricating process could be expressed by Fig. 2. Firstly, evacuation of the tube was performed by Ar gas flow for one hour. Then the temperature of the furnace was ramped up to 1000° C at a rate of 20° C per minute. For avoiding or minimizing the oxidation, Ar gas flow was maintained in the chamber in this process. When the temperature reached to TC (1000ºC, 950ºC, 900ºC, 850ºC respectively), both $SiCl_4$ (10 sccm) and $GeCl_4$ (10 sccm) were introduced into the chamber with H2 (100 sccm) flows for certain times as precursors. After finishing the fabrication, the $SiCl_4$, $GeCl_4$ and H_2 supply was turned off and the temperature was allowed to go down for the coming experiments by maintaining Ar gas flow into the chamber in this process for avoiding or minimizing oxidation.

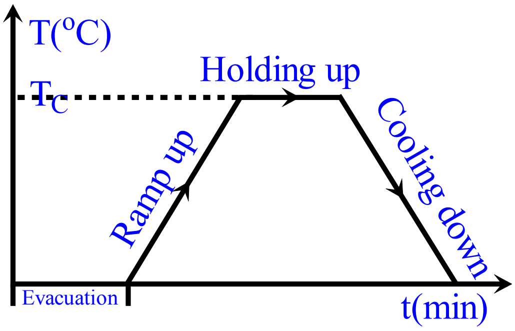

Fig. 2: The experimental process for the three steps distribution in the tube furnace showing evacuation to ramping up and finally cooling down in the chamber.

In our experiments, $SiCl_4$ and $GeCl_4$ were used as precursors for Si and Ge of the fabricated SGNWs respectively, and the SGNWs were grown successfully at a temperature of 1000ºC. The mole ratios of precursors ($SiCl_4$: $GeCl_4$) could be controlled as 2:8, 3:7, 4:6, 5:5, 6:4, 7:3 and 8:2 respectively, and the corresponding growth time as 8, 5 and 10 minutes respectively.

Parts of the resulted SGNWs (mole ratios of 5:5 for 8 min, 2:8 for 5 min, 8:2 for 10 and 5 min) are shown in Fig. 3 by the SEM images in different scales and the photographs respectively. We can observe that the vertical SGNWs could be grown successfully at all of the three different selected compositions for different times under 1000ºC. The lengths of the formed SGNWs could

be controlled easily by controlling the growth time, and the composition of the SGNWs could also be modulated by the flowing mole ratio of the precursors very easily.

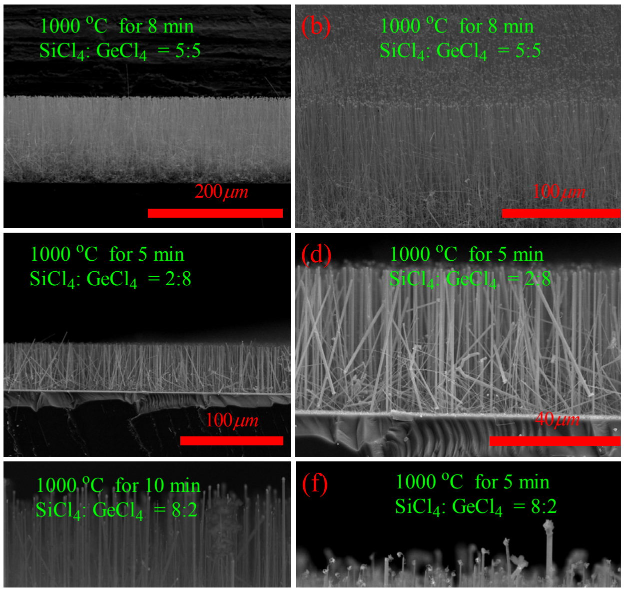

Fig. 3:SEM images of the fabricated SGNWs sample under 1000ºC. (a) (b) Crosssection of the fabricated SGNWs under precursor's flowing mole ratio of 5:5 ($SiCl_4$: $GeCl_4$) for the growth time of 8 minutes. (c) (d) The precursor's flowing mole ratio is 2:8 ($SiCl_4$: $GeCl_4$) for the growth time of 5 minutes. (e) (f) The precursor's flowing mole ratio is 8:2 at sccm ($SiCl_4$: $GeCl_4$) for the growth time of 10 and 5 minutes respectively.

These results show that the change in time and compositions did not affect the vertical growth ability of NWs.

The composition distributions of the fabricated SGNWs fabricated under 1000ºC with $SiCl_4$:$GeCl_4$=08/02 for 10 min are shown in Fig. 4 analyzed by TEM, which shows that the composition of the fabricated SGNWs is compatible with the amount of the used precursors (the Si element content is higher than that of Ge element). However, the concrete content of the Si and Ge elements would be changed in different positions of the fabricated SGNWs. We cannot observe the Ni element on top of the fabricated SGNWs and bottom of the fabricated SGNWs, but just exist in the neck of the NWs. And the Si element content on the top of the fabricated SGNWs is comparatively less compared to that in the neck and bottom of fabricated SGNWs.

In our experiments, the temperature effect was also analyzed by varying the circumstance temperature in the tube furnace in the fabricating process at four different

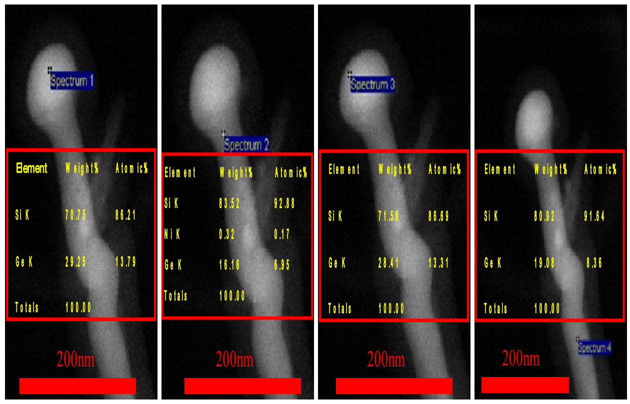

Fig. 4: The TEM images showing composition distribution in different positions of the SGNWs fabricated under 1000º C with $SiCl_4$:GeCl4=08/02 for 10 min

positions of 850º C, 900ºC, 950ºC and 1000ºC. The wires were grown successfully at all these temperatures, although some of the nanowires were grown in flower

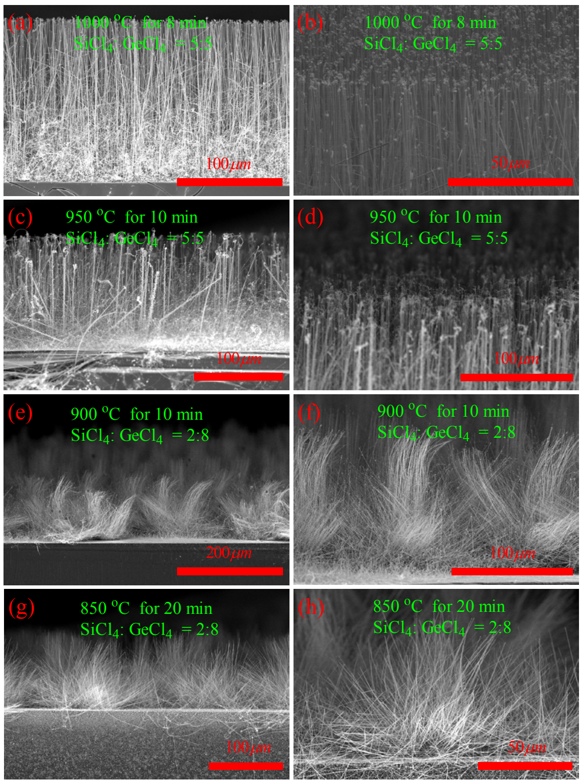

Fig. 5: SEM images and the photographs of SGNWs sample under different fabricating temperatures. (a) (b) The precursor's flowing mole ratio is 5:5 at sccm ($SiCl_4$: $GeCl_4$) for the growth time of 8 minutes under temperature of 1000ºC. (c) (d) The precursor's flowing mole ratio is 5:5 at sccm ($SiCl_4$: $GeCl_4$) for the growth time of 10 minutes under temperature of 950ºC. (e) (f) The precursor's flowing mole ratio is 2:8 at sccm ($SiCl_4$: $GeCl_4$) for the growth time of 15 minutes under temperature of 900ºC. (g)(h) The precursor's flowing mole ratio is 8:2 at sccm ($SiCl_4$: $GeCl_4$) for the growth time of 15 minutes under temperature of 850ºC.

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like structure at 850° C and 900° C as depicted in Fig. 5. It was observed that the wires were vertical and with more uniform structure at a temperature of 1000°C as shown in Fig. 5 (a-b). However, with the decrease of the circumstance temperature to 950°C, the uniformity of the NWs is decreased and some parts of the NWs are not vertical as shown in Fig. 5 (c-d) compared to Fig. 5 (a-b). With the decrease of the circumstance temperature to 900°C and 850°C, as shown in Fig. 5 (e-f) and Fig. 5 (g-h) respectively, the fabricated SGNWs lose the uniformity absolutely and there is no NWs remaining vertical characteristics nearly, and the resulted SGNWs look like some special flowers.

With increasing the length of the resulted SGNWs, the color of the samples changed from faint yellow to dark yellow and brown, which means that the optical property of the SGNWs would be affected by the length greatly. And this optical characteristic could be further proved by the measured total reflection (R) and the transmission (T) of the fabricated SGNWs, which shows the fabricated SGNWs, could be used for the solar cell applications.

Conclusion

In conclusion, $Si_{1-x}Ge_x$ nanowires were gently grown axially by means of VLS technique with change in their compositions with a $SiCl_4$: $GeCl_4$ ratio of 2:8, 3:7, 4:6, 5:5, 8:2, 7:3 and 6:4 respectively. The growth was carried out for different times and different temperatures including 1000°C, 950°C, 900°C and 850oC. It was found that the nanowires were grown successfully vertical on almost all temperatures except at 900°C and 850°C, some of the wires were observed as bearing flower like structure. The optical characteristics of the resulted NWs show the great potential in the application of solar cell.

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