Influence of Fe Films in the Growth of Carbon Nanotubes by Chemical Vapor Deposition

Hui Li*
Shanxi engineering research center of controllable neutron source, Xijing University, Xi’an, 710123, China
*Corresponding Author Email: lzlihui@163.com

Abstract: The metal catalyst plays an important role in the preparation of carbon nanotubes (CNTs). In this work, we prepared Fe film catalyst layer by electron beam evaporation method, and studied its influence in the growth process of CNTs by chemical vapor deposition (CVD) method via adjusting the thickness of layer, annealing temperature and annealing time. The obtained results demonstrate that the thickness, annealing temperature and annealing time of catalyst layer play significant role in the growth of CNTs. Under the same growth condition, the longest CNTs (about 234µm) can be obtained when the 2nm thick Fe catalyst layer was annealed at 700°C for 10min. These results provide a certain research basis for the related application filed of CNTs.

1. Introduction
Over the past 30 years, carbon nanotubes (CNTs) have been widely concerned by researchers due to their small size, large specific surface area, unique electronic characteristics, and relatively high chemical properties [1-3]. The outstanding mechanical, electrical, thermal and biochemical properties of CNTs have great application potential in many fields, such as nanoelectronics, quantum wire interconnection technology, biosensors, metal and ceramic compounds and field emission devices etc. [4-6]

Although many methods have been used for the growth of CNTs [1, 7-8], the preparation of large-area, orderly and controllable growth CNTs arrays is still a great challenge [9-11]. Among the currently reported methods for growing CNTs, thermal chemical vapor deposition(TCVD) and plasma enhanced chemical vapor deposition (PECVD) are the most commonly used and effective methods. However, after many years of research, a basic problem still exists in the growth of CNTs by CVD, that is, the effect of catalyst parameters on the growth of CNTs is still unknown [12-14].

As the nucleation center and energy transporter of CNTs, the selection and preparation of CNTs catalyst have great influence on the nucleation, growth rate and density of CNTs, which will lead to different shapes and structures of CNTs [14-15]. In the growth of CNTs, the most suitable catalysts are the transition metals Fe, Co and Ni, because these transition metals have high carbon dissolving power and can form certain carbides. Most CNTs arrays are also fabricated using these metal catalysts [16-19]. The parameters of the catalyst have a significant influence on the final CNTs. For example, the particle size of the catalyst determines the diameter of the CNTs.

In this paper, we select the catalyst Fe as the research object. The Fe layers with different thickness was prepared by electron beam evaporation and annealed. The effects of the thickness of catalyst layer, annealing temperature and time on the growth of CNNS were studied by changing the annealing temperature and time.
2. The Experimental
Tube furnace chemical vapor deposition systems (including a 4-inch quartz tube furnace, mass flow meter, and gas path system) are used to complete the fabrication of CNTs on a silicon substrate.

Firstly, the substrate Si wafer (4 inches in diameter) was washed in a mixed solution of concentrated H₂SO₄ and H₂O₂ (V: V =3:1) at 120°C to remove the metal and organic impurities on the surface. Then, it is processed in a high-temperature oxidation furnace to prepare a layer of SiO₂ with a thickness of 2μm to prevent the catalyst from diffusing to the Si substrate. Moreover, metallic Fe film of 2-10nm thick was deposited on the SiO₂ layer. Finally, the silicon substrate with the catalytic layer was cut into small pieces of 2cm×2cm in size and placed in a quartz tube furnace for subsequent processing.

Before the growth of CNTs, the deposited Fe film of catalyst will be pre-annealed for a certain period of time under atmosphere. The morphology of the catalyst Fe film and the grown CNTs were characterized by scanning electron microscope (SEM) and atomic force microscope (AFM).

3. Experimental Analysis and Diagrams
In order to study the effect of the thickness of the catalytic layer on the growth of CNTs, we used electron beam evaporation to deposit Fe thin films with different thickness (2, 5, 10nm, respectively). After deposition, annealing was performed in H₂ atmosphere for 15min to obtain the catalyst Fe. The surface topography of the film was shown in Fig1.

![Figure 1. The Fe film morphology surface of different thickness (a)2nm (b)5nm (c)10nm after annealing at the temperature of 700°C](image)

As can be seen from Fig1, the Fe films tend to agglomerate to form nanoparticle due to the high surface tension during annealing. With the increase of the thickness of Fe film, the diameter of Fe particles increases and the density of Fe particles decreases.

After determining the effect of film thickness on the catalytic particles, the next step is to study the effect of annealing temperature on the catalytic particles. We selected an Fe catalyst layer with a thickness of 2nm and a fixed annealing time of 10 min. Fig.2 and 3 show the effect of annealing on the Fe surface and Fe particle size of the catalyst, respectively. From Fig2(a), it can be found that before annealing, the surface of the deposited Fe film is very smooth, without obvious graininess.
After annealing at 700°C, protrusions began to appear on the surface of the catalyst film, and the film began to form a granular structure (see Fig2b). This was because the high temperature caused the tension of the Fe film to increase, and the film layer differentiates into islands isolated from each other, thereby forming a particle structure. The appearance of the particle structure reduces the density of the catalyst particles, but its uniform distribution is relatively uniform. After annealing at 800°C and 900°C (as shown in Fig2c and 2d), the density of the Fe particles of the catalyst further decreases and the distribution becomes less uniform, which will cause the density of the final grown CNTs to become sparse.

Fig3 showed the changes of the root mean square roughness of the catalyst film surface and the diameter of the particles with the annealing temperature. It was found that as the annealing temperature increased, the root mean square roughness of the film surface and the average diameter of the catalyst particles increased simultaneously. This was because after the film was annealed, the mobility of the surface particles increased, which would agglomerate or merge to form larger particles to reduce the surface energy and coalescence. This coalescence phenomenon promoted the formation of large catalyst particles, which reduced the density of the catalyst particles and resulted in uneven distribution. However, because of the small diameter of the CNTs it was difficult to directly relate the diameter of the grown CNTs to the measured diameter of the CNTs.

This is because at high temperatures the density of catalyst particles decreased (800°C and 900°C are more obvious) and the high reaction rate made the carbon dissolution, diffusion, and precipitation phenomena impossible to be ignored. These effects caused by high temperature will absorb more carbon atoms, increase the diffusion rate, produce large-diameter CNTs and reduce the growth density of CNTs.
Next, we will focus on the effect of annealing time on the morphology of the catalyst film (at this time the annealing temperature was maintained at 700°C), the specific experimental results were shown in Fig4 and Fig5.

It can be seen from the Fig4 that the surface of Fe films annealed for 5 minutes had obvious interface with the unannealed films (comparison with Fig2a). As the annealing time increases to 10 minutes, the surface of the film begins to appear uneven, resulting in a small amount of agglomeration. When the annealing time was further increased to 20 or 30 minutes, the agglomeration phenomenon was significantly enhanced, and the granular characteristics of the catalyst increased. The above results indicate that as the annealing time increases, the catalyst particles will form aggregates to reduce the surface energy [20].

Fig5 showed the simple relationship between the annealing time of the catalytic layer and the length of the grown CNTs. It can be found that after 5 minutes of annealing treatment the vertical length of CNTs is only 134μm, and after 10 minutes of annealing treatment the length of the grown CNTs increases to 234μm. This is because the annealing time of 5 min is not enough to form Fe catalytic particles. After 10 minutes of annealing, the distribution and density of Fe particles are in a relatively suitable state, and the length of CNTs increases to 234μm. As the annealing time continues to increase, the length of the grown CNTs begins to decrease. For example, the length of CNT prepared after 15 minutes of annealing has begun to decrease to 200μm, while after 30 minutes annealing the length of grown CNT has dropped to less than 100μm. For this phenomenon, we believe that the annealing time of the catalyst causes the increase of the average particle size and reduces the distribution density of the particles. Among them, the complex growth mechanism and physical model need further research.

![Figure 4. SEM pictures of the catalyst film at different annealing times (a)5min (b)10min(c)20min(d)30min](image)

![Figure 5. The CNTs lengths varying different annealing times after Fe catalyst annealed at 700°C](image)
4. Conclusion
In this paper, the effect of the change of catalyst Fe film parameters on the final length of CNTs grown by CVD method was studied. The results showed that the length of the grown CNTs was closely related to the thickness of the catalyst film, pre-annealing temperature and pre-annealing time. Comprehensive experimental results showed that the length of the prepared CNTs was optimal prepared at the 2nm-thick Fe film deposited by electron beam evaporation annealing at 700°C for 10 minutes.

5. References
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