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Study on the spinnable carbon nanotube arrays prepared by chemical vapor deposition

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The purpose of this research was to establish spinnable carbon nanotube(CNT) arrays. A carbon nanotube array with a certain height and good alignment was grown by chemical vapor deposition, it was applied to use dry spinning method to prepare CNTs fiber. In this study, CNT arrays were grown by two different processes, thermal chemical vapor deposition and floating catalyst chemical vapor deposition. Electron beam evaporation technology was used to deposit the iron layer and ferrocene powder as the catalyst. By controlling the gas volume flow, reaction temperature and other parameters in the process to control the growth of CNTs. The research results show that CNTs grown by floating catalyst chemical vapor deposition can get better results. By changing the evaporation temperature of ferrocene powder, CNT array of better quality can be grown. When the ferrocene vaporization temperature was 360 ℃, the C2H2 flow rate was 15 sccm, the H2 flow rate was 60 sccm, the H2 pre-treatment time was 4 min, and the reaction temperature was 770 ℃ for 15 min, the height of CNT arrays can reach 568 μm.

NOMENCLATURE

A: Ferrocene evaporation temperature (°C)
B: C_2H_2 flow rate (sccm)
C: H_2 flow rate (sccm)
D: H_2 pre-treatment time (min)

1. Introduction

Carbon nanotubes(CNTs) were micro-nanoscale non-metallic materials. Because of their good electrical conductivity, mechanical strength and other advantages, they have great development prospects[1]. Because the scale of carbon nanotubes was too small, they can bring excellent performance into the macro field. Therefore, the research on the preparation of CNT arrays came into being. The CNT arrays can make better use of carbon nanotubes at the macro level. Related properties of the CNTs, such as: preparing CNT fibers, as a field emission tip, as a conductive medium in the sensor[2].

Among them, the preparation of CNT fibers can be obtained by two methods: dry spinning method and wet spinning method, which belong to physical methods and chemical methods, respectively. In 2007, Zhang et al. obtained high-strength CNT fibers by pulling CNTs sheet from a well-arranged CNT array and twisting them to better maintain the appearance of CNTs and related properties[3]. In contrast, the dry spinning method uses surfactants to combine with CNTs to undergo a chemical reaction, resulting in degradation of the related properties of the surface morphology [4].

Therefore, the dry spinning method was a better method for preparing CNT fibers. To obtain a spinnable CNT array, the CNT array was required to have good alignment, high purity, and sufficient height. The method uses a chemical vapor deposition(CVD) to cause a chemical reaction between the catalyst and the carbon source gas under high temperature conditions to grow CNT arrays. Spinnable CNT arrays were originally proposed by Jiang et al. in 2002. They grow a cluster of CNT arrays with a height of several hundred microns on a 1 cm^2 silicon substrate, and used tweezers to continuously pull them from the side. In the end, a CNT sheet with a length of about 10 m was obtained, and the spinnability of CNTs was realized for the first time[5]. And with the gradual maturity of research methods, how to improve the height and quality of spinnable CNT arrays has become a key issue for researchers. In 2010, Kim et al. studied the film thickness, annealing time, and grow temperature parameters of the iron catalyst during the thermal chemical vapor deposition(TCVD) process and found that changing the parameters can change the distribution of iron catalyst particles, thereby indirectly controlling the growth of CNT arrays[6]. In addition, Zhang et al. in 2017 found that the difference in the surface morphology of the buffer layer deposited under the catalyst layer will also affect the diffusion and nucleation of the upper catalyst particles[7].

With the gradual maturity of the CNT array manufacturing

process, many researchers have discovered that the use of iron as a catalyst layer was prone to oxidation and cannot effectively keep the catalyst activity. Therefore, choosing a catalyst with higher activity becomes a more important change in the quality of the process. An effective method, the floating catalyst chemical vapor deposition(FCCVD) came into being. In 2017, Hoecker used ferrocene powder directly as a catalyst, using it would evaporate at 250 °C to form supersaturated steam, and enter the reaction chamber together with the carbon source gas, to grow the CNTs at a temperature higher than 600 °C [8].By using ferrocene as a catalyst, it avoided the metal catalyst layer was exposed to the air for too long in the process of depositing the catalyst layer by external sputtering or evaporation, which will cause the oxidation of the catalyst layer. Use FCCVD, the deposition method effectively circumvents other variables and avoids the decrease of catalyst activity [9].

Therefore, in this study, the traditional TCVD and the FCCVD are used to prepare CNT arrays. It hoped that the process steps for spinning CNT arrays would be established, and the growth of CNT arrays would have a certain height and good growth. By improving the type of catalyst, using ferrocene powder directly as a catalyst, and by controlling the evaporation temperature of the ferrocene powder, a better-quality CNT array could be grown.

2. Experiment process

2.1 TCVD

When using the TCVD to grow CNT arrays, a silicon wafer with a layer of 500 nm SiO_2 on the top was selected as the substrate, and an Al_2O_3 buffer layer and Fe catalyst layer were deposited by electron beam evaporation technology. The vapor-deposited substrate was broken into 1 cm^2 test pieces to prepare for the experiment. The growing CNT array was carried out using a 1-inch high-temperature furnace tube. First, 300 sccm of He and 200 sccm of Ar were aerated for 10 min of gas replacement. Then the furnace was heated to 720℃ within 20 min at a position far from the test piece, while He and Ar were aerated continuously. A slide rail was attached under the furnace to make it move to our desire position from the test piece. When the desire temperature was achieved, the furnace was quickly moved along the slide rail to the reaction area where the test piece was located, and the test piece would quickly stabilize to 720 ℃ within 8 min. At the same time, the Ar was turned off and 80 sccm of H_2 was introduced to anneal the catalyst substrate. After the annealing was completed, 20 sccm of C_2H_2 was introduced to grow the CNT array for 10 min. After the reaction over, the reaction gas was turned off, He and Ar were continuously fed in until the temperature drops to 100°C.

2.2 FCCVD

When using FCCVD to grow CNT arrays, a silicon wafer with a layer of 500 nm SiO_2 on the top was selected as the substrate, and 45 nm Al_2O_3 was evaporated as a buffer layer. The schematic diagram of the experiment was shown in Fig. 1. The test piece and 0.03 g of ferrocene were placed in the furnace tube, and the evaporation temperature of the ferrocene powder was controlled by changing the position where the ferrocene powder was placed in the furnace tube. Then pass in 300 sccm of He and 200 sccm of Ar for 10 min gas replacement. Then carry out a 20 min heating step. After that, move the furnace along the lower slide rail to the reaction area where the test piece was located, turn off Ar, and pass in 60/80/100 sccm H_2 for 4/6/8 min pretreatment. Finally, introduced 15/20/25 sccm C_2H_2 for 15 min to grow CNT array. After the reaction was over, the reaction gas was turned off, He and Ar were continuously introduced until the temperature drops to 100°C.

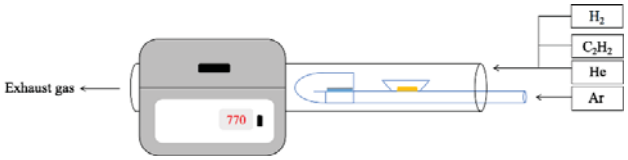

Fig. 1. Schematic of CNT array grown by FCCVD.

The Taguchi method was selected for experimental design when the experiment was carried out by FCCVD. In this study, the factors affecting the experimental results were, A means the evaporation temperature of ferrocene, B means C_2H_2 flow rate, C means H_2 flow rate, D means H_2 pretreatment time, each factor was set separately. There were 3 different levels. Table 1 was a table of the factor parameters that affect the experiment.

According to the Taguchi method, the $L_9(3^4)$ Taguchi orthograph table was selected as shown in Table 2. A total of 9 sets of experiments were performed, and each set of experiments was repeated 3 times. The height of the CNT array and the I_D/I_G value were used as the observation values. Analyze them separately to find out the important factors that affect the experimental results[10].

Table 1 The factor parameter table of influences the experiment.

Factor	1	2	3
A: Ferrocene evaporation temperature (°C)	360	380	400
B: C_2H_2 flow rate (sccm)	15	20	25
C: H_2 flow rate (sccm)	60	80	100
D: H_2 pre-treatment time (min)	4	6	8

Table 2 Experimental groups planned according to Taguchi Method.

No.	A	B	C	D
1	360 °C	15 sccm	60 sccm	4 min
2	360 °C	20 sccm	80 sccm	6 min
3	360 °C	25 sccm	100 sccm	8 min
4	380 °C	15 sccm	80 sccm	8 min
5	380 °C	20 sccm	100 sccm	4 min
6	380 °C	25 sccm	60 sccm	6 min
7	400 °C	15 sccm	100 sccm	6 min
8	400 °C	20 sccm	60 sccm	8 min
9	400 °C	25 sccm	80 sccm	4 min

3. Conclusions

In this study, a 1-inch furnace tube was used to grow CNT arrays by CVD using two different catalysts. When using electron beam evaporation technology to deposit an iron film as a catalyst, the method grown CNT arrays called TCVD. In this method, CNT arrays with a height of about 123 μm can be obtained, when the growth temperature was 720 ℃ for 10 min. When ferrocene powder was used as a catalyst, the position of the ferrocene powder was changed by FCCVD to control the evaporation temperature of the ferrocene. So, in this method, we could obtain CNT array with good quality and height. The CNT array was pre-treated at a ferrocene evaporation temperature of 360 ℃, 60 sccm of H_2 was used, and pretreated for 4 min, and then 15 sccm of C_2H_2 was injected and grown at a growth temperature of 770 ℃ for 15 min. The height of CNT array can reach 568 μm and with high crystallinity.

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