

# Layered growth of aligned carbon nanotubes arrays on silicon wafers

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## Abstract

Aligned carbon nanotube arrays were synthesized on Fe-coated Si substrates using thermal chemical vapor deposition (TCVD) method by pyrolysis of  $C_2H_2$ . The results show that carbon nanotube arrays with two layers were obtained after growth for 60 min, which were connected to each other through iron catalyst particles. A possible growth model for the layered carbon nanotube arrays is proposed. In addition, the results show that the time of catalyst pretreatment in  $NH_3$  affected greatly the morphologies of the layered carbon nanotube arrays and the reason for this was discussed.

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*Keywords:* Aligned CNTs; Chemical vapor deposition; Microstructure; Ammonia treatment

## 1. Introduction

Since their discovery [1,2], carbon nanotubes (CNTs) have attracted much attention because of their unique physical and chemical properties and their potential applications [3–5]. The large aspect ratio of CNTs together with their small tip radii of curvature, high chemical stability, thermal conductivity and high mechanical strength are advantageous for applications to the field emitter. Several results have been reported on the field emission from multi-walled nanotubes (MWNTs) and single-walled nanotubes (SWNTs) [6,7] and demonstrated that they are the most efficient electron emitter among various materials. In the practical application of carbon nanotubes as field electron sources, aligned carbon nanotubes should be grown in a large area.

Alignment of carbon nanotubes was first made by means of two kinds of post-growth methods [8,9]. In 1996, Li et al. [10] firstly reported the growth of carbon nanotube arrays using iron catalyst embedded in porous silica. After that, several works on the growth of aligned carbon nanotube arrays [11–14] have been reported. These carbon nanotube arrays were synthesized on various kinds of substrates, such as on porous silica [11], silicon [12], porous silicon [13] or glass [14] and the catalyst are

Fe, Ni, or Co, respectively [15–17]. Because carbon nanotube arrays are important both for fundamental studies and application, there was a lot of work focused on this topic recently with different production methods [18–20]. In all the synthesis methods, chemical vapor deposition (CVD) seems to be the most promising method for producing aligned carbon nanotube arrays.

CVD method was used to synthesize aligned carbon nanotubes and has produced a multitude of novel shapes such as nanosprings [21], bamboo trunks [22], and connectors [23] under different processing conditions. Recently, Zhang et al. [24] synthesized layered aligned carbon nanotube arrays by pyrolysis of ferrocene in xylene. They believed that the continuous feeding of the catalyst precursor plays a critical role in the growth of the layered carbon nanotube arrays. Sun et al. [25] also prepared layered carbon nanotube arrays using the existing array as a substrate. However, during our experiment the layered carbon nanotube arrays were fabricated on plain Si substrate coated with iron films using TCVD method. In this paper, a possible growth model for the layered carbon nanotube arrays and the effect of catalyst pretreatment in  $NH_3$  on the morphologies of carbon nanotube arrays were discussed.

## 2. Experimental

Aligned carbon nanotube arrays were grown using thermal decomposition of  $C_2H_2$  at atmospheric pressure. N-type silicon

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(111) wafers with a resistivity of 4–4.8  $\Omega$  cm were used as substrates. Five nanometers of Fe films were deposited on the substrates by a metal vapor vacuum arc (MEVVA) ion deposition system. Before deposition, the substrates were bombed by Fe ion to obtain clean surface. The synthesis of CNT arrays was carried out in a horizontal TCVD system. The as-prepared Si substrates were placed in the reaction region of a horizontal quartz tube furnace. The reaction region was heated to 580  $^{\circ}$ C under nitrogen and then nitrogen substituted by hydrogen at a flow rate of 400 ml/min to deoxidize the Fe catalyst for 30 min. After that, the reaction region was heated to the synthesis temperature (750  $^{\circ}$ C) in hydrogen. Prior to decomposition reaction, Fe catalyst on Si substrates was pretreated in  $\text{NH}_3$  gas. Subsequently a mixture of  $\text{H}_2$  and  $\text{C}_2\text{H}_2$  at the ratio of 70/400 ml/min was introduced into the reaction region. The catalytic decomposition reaction proceeded for 60 min. The samples were cooled to room temperature by the in-flow of  $\text{N}_2$  and then taken out. During the growth process of carbon nanotubes,  $\text{H}_2$  served as etchant and dilute gas. The purities of the gas employed in the experiment are all higher than 99.5%. The time of catalyst pretreatment in  $\text{NH}_3$  was varied to study its influence on the morphologies of layered carbon nanotube arrays.

Field emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM) were used to observe the microstructures and morphologies of aligned carbon nanotube arrays and catalyst films. Energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) analysis were used to determine the elemental compositions of the samples.

### 3. Results and discussion

Fig. 1 shows the FESEM images of the layered carbon nanotube arrays synthesized after pretreatment of Fe catalyst in  $\text{NH}_3$  for 12 min. From Fig. 1 study, it can be seen that the nanotubes with the diameters centered at around 40 nm are aligned but seriously curved and their total length is about 30  $\mu\text{m}$ . A boundary that separated the array into two layers is clearly visible and the heights for the bottom and top layer are about 20 and 10  $\mu\text{m}$ , respectively. However, a little amorphous carbon particles and fibers were found in the carbon nanotube arrays. Fig. 1(b) is a close view of the interface in Fig. 1(a), in which the carbon nanotubes are unaligned. The carbon nanotubes are sharply bent (as shown in Fig. 1(c)). EDX analysis shows the rich Fe element in the interface.

As the time of catalyst pretreatment in  $\text{NH}_3$  decreased to 10 min, a layered carbon nanotube array with the similar structures was obtained (as shown in Fig. 2) following the same procedure. However, the total height of the carbon nanotube array is increased to about 100  $\mu\text{m}$  during the same growth time, and about three times as that seen in Fig. 1. But the top layer is still around 10  $\mu\text{m}$ . The average diameter also is increased to about 85 nm. And the carbon nanotube array has a better alignment. From Fig. 2(b), Fe catalyst particles are cylindrical and encapsulated in the carbon nanotubes, which were identified by the EDX analysis. Fig. 2(c) shows the tips of carbon nanotubes with various shapes such as closed (arrow 2), opened (arrow 1) and conical shape (arrow 3).

With the time of  $\text{NH}_3$  pretreatment continuously decreased to 8 min, the phenomenon of layered growth of the carbon nanotube

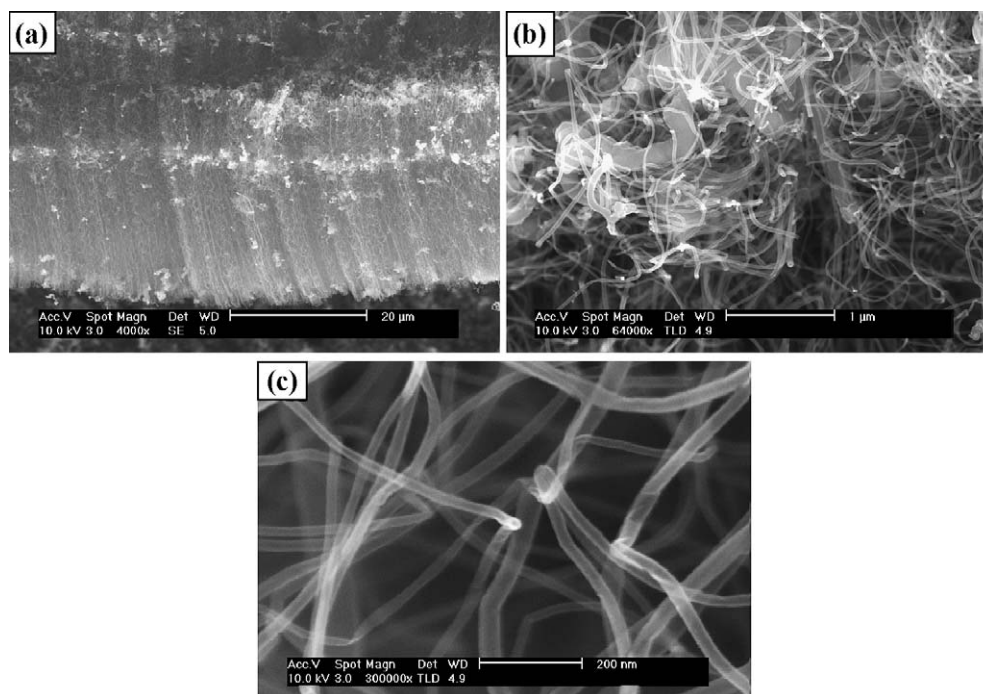


Fig. 1. Morphologies of layered carbon nanotube arrays synthesized when the catalyst was pretreated in  $\text{NH}_3$  for 12 min: (a) low magnification of the layered carbon nanotube arrays; (b) interface between the two layers; (c) high magnification of the interface.

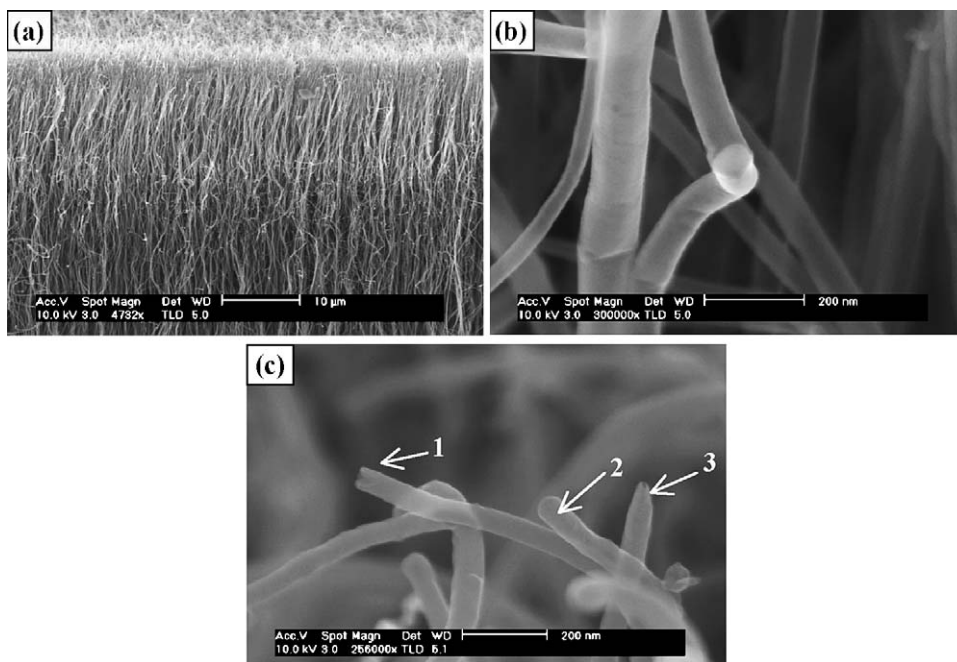


Fig. 2. Morphologies of layered carbon nanotube arrays synthesized when the catalyst was pretreated in  $\text{NH}_3$  for 10 min: (a) a view of the interface between two layers; (b) high magnification of the interface; (c) morphologies of the carbon nanotube tips.

array is still obvious (as shown in Fig. 3). From the analysis of Fig. 3, most of the carbon nanotubes terminated in the interface and the others continued to grow. Consequently, a carbon nanotube array with two layers was obtained and the density of the top layer decreased. The heights of both layers also slightly decreased. And many carbon nanofibers and amorphous carbon particles turned up in the upper of the top layer. EDX analysis in the interface shows the catalyst particles are encapsulated in

the carbon nanotubes. From Fig. 3(c), a small branching carbon nanotube grew from the outer wall of the carbon nanotube. However, no layered carbon nanotube arrays were obtained when the Fe catalyst was not pretreated in  $\text{NH}_3$ , or Co/Si and Ni/Si were used as catalyst following the same procedure.

With regard to the growth models for carbon nanotubes, the tip growth model [18] and base growth model [22] were proposed previously. Recently, the combination of base-growth and

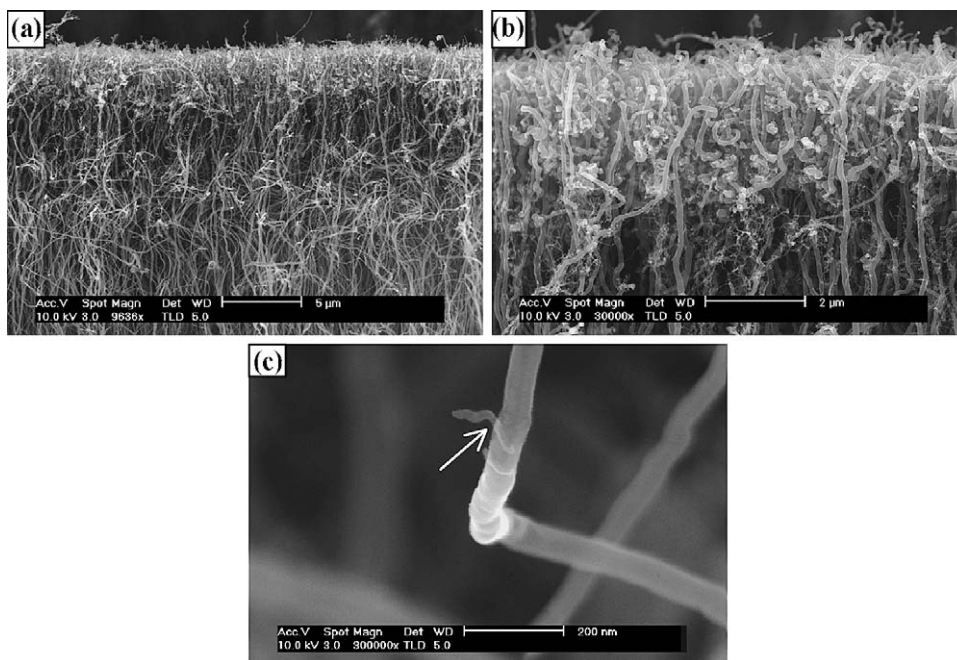


Fig. 3. Morphologies of layered carbon nanotube arrays synthesized when the catalyst was pretreated in  $\text{NH}_3$  for 8 min: (a) a view of the interface; (b) upper morphologies of the above layer; (c) a small branching carbon nanotube grew from the outer surface of the carbon nanotube.

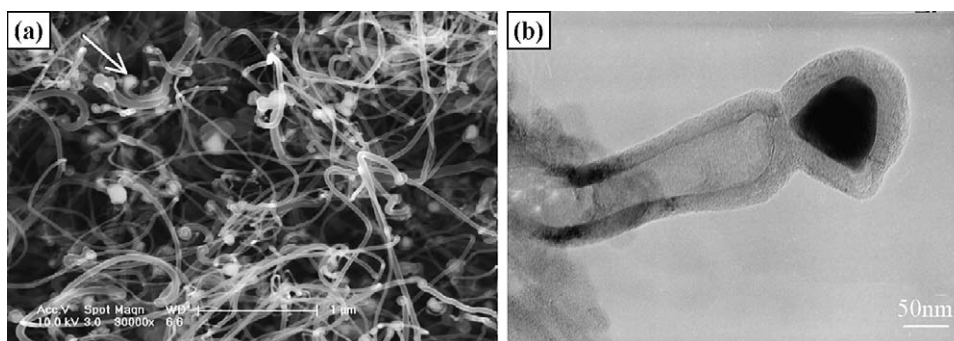


Fig. 4. (a) SEM image of the top of aligned carbon nanotube arrays synthesized for 30 min; (b) HRTEM image of the tip of the carbon nanotubes synthesized for 45 min.

tip-growth for a single nanotube structure has efficiently introduced [26] using organic-metallic as catalyst precursors through successive feeding. According to the characteristics of the carbon nanotube arrays obtained in our experiment, the tip-growth and base-growth models should be responsible for the growth of the bottom and top carbon nanotube layer, respectively.

Fig. 4(a) is the top view of the carbon nanotube arrays after synthesis for 30 min. It is clearly seen that many catalyst particles were encapsulated in the tip of carbon nanotubes, which further demonstrated that the bottom carbon nanotube layer grown according to the tip growth-model. During the growth process, hydrogen, serving as etchant gas, kept the top of the catalyst clean and provided an adsorption pathway of carbon atoms. When graphite layers grew along the particle surface, the particles would be thinned (as shown in Fig. 4(a), arrow points) so that they were cylindrical (as shown in Fig. 2(b)).

As the growth of the carbon nanotube proceeds, the growth rate of the carbon nanotubes decreased possibly due to gradual deactivation of the catalyst. Catalyst deactivation may be caused by one or a combination of the following three mechanisms [27]: a decrease of the number of active sites, a decrease in the quality of the active sites, and a degradation in accessibility. The growth process of carbon nanotubes includes three stages: adsorption of carbon atoms decomposed from  $C_2H_2$  on the surface of catalyst, diffusion of carbon atoms through the surface or bulk of the catalyst particles due to the concentration gradient of carbon atoms and extrusion of carbon at the active sites in the form of C-hexagon.

At the fixed temperature, the decomposition rate of  $C_2H_2$  into carbon atoms is constant and hence the supply and adsorption of carbon atoms are not the limited factors for the growth of carbon nanotubes. However, with the growth proceeding, the quality of the active growth sites, where the carbon nanotubes were growing, might decrease gradually and hence prevented the extrusion of carbon in the form of C-hexagon. The carbon atoms dissolved in the catalyst might continuously extrude from the bottom of the catalyst particle and formed an amorphous C-layer (as shown in Fig. 4(b)). Fig. 4(b) shows the HRTEM image of the carbon nanotube tip after growth for 45 min. It is clearly seen that a thick carbon layer formed under the catalyst particles. The carbon layer finally may further stop the extrusion of carbon atoms with increasing its thickness.

At the same time, the carbon atoms concentration gradient in the catalyst also decreased and therefore their diffusion rates due to a decrease in the extrusion rates of carbon. The excess carbon adsorbed on the surface of catalyst would accumulate and form continuous or incontinuous carbon layers on the top of catalyst particles, which hindered the dissolving of carbon atoms and further prevented the growth of the carbon nanotubes. Therefore, with increasing growth time, the growth rate of the carbon nanotubes decreased gradually.

With the growth time increased, the carbon atoms dissolved in catalyst should extrude from the new active sites of the catalyst particles. It could induce the nucleation and growth of the new carbon nanotubes from the catalyst particles. The catalyst particles on the top of the carbon nanotubes cannot freely move along the inner tube walls, which are in close contact with them. Therefore, with the adding of carbon to the edge under the as-formed carbon layers on the top of the catalyst particles, they lifted off the catalyst particles and carbon nanotube tips with various kinds of shapes were formed (as shown in Fig. 2(d)). Accordingly, the new carbon nanotube grew abiding by the base growth model and formed the top layer in the original carbon nanotube arrays, which were connected with the as-formed bottom carbon nanotube layer through the catalyst particles encapsulated in the carbon nanotubes. The small branching carbon nanotubes in Fig. 3(c) grew from the outer wall of the carbon nanotube where the catalyst particle was encapsulated, which further demonstrated the presence of the new active growth sites for the carbon nanotubes on the catalyst. However, with increasing growth time, the new growth sites on the catalyst particles were deactivated again and amorphous carbon fibers and carbon particles turned up on the top of carbon nanotube arrays (as shown in Fig. 3(b)).

According to the above results, since the above carbon nanotube arrays were synthesized using the same synthesis procedure, their different morphologies should be ascribed to the various time of the catalyst pretreatment in  $NH_3$ . Therefore, in order to elucidate the influence of the time of the Fe catalyst pretreatment on the morphologies of the carbon nanotube array, Fe catalyst after pretreatment in  $NH_3$  for varied time was investigated. The relations between the size and density of catalyst particles and the duration of catalyst pretreatment were described in Fig. 5. With increasing duration of catalyst

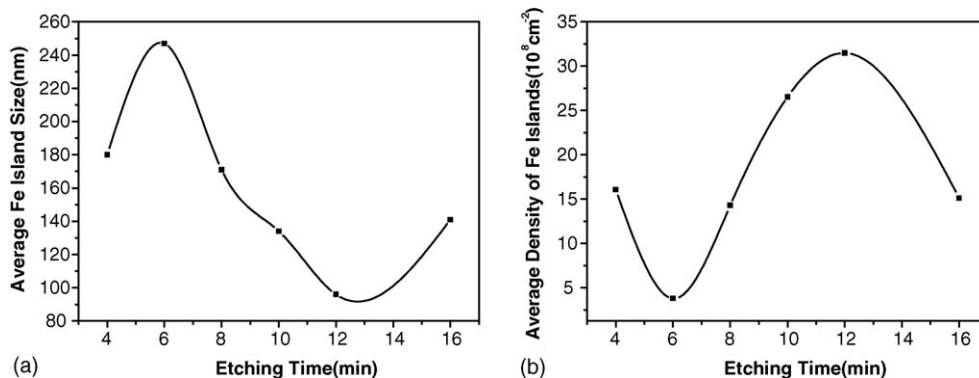


Fig. 5. Influence of the duration of  $\text{NH}_3$  pretreatment on the Fe particle size (a) and density (b) of 5 nm Fe film.

film pretreatment in  $\text{NH}_3$ , the mean catalyst particle size first increased and then decreased, lastly increased rapidly. On the contrary the corresponding average density of catalyst particles first decreased and then increased, lastly decreased again. And the density of the catalyst particles increased greatly with the duration of pretreatment increased from 6 to 10 min, and then began to increase slowly from 10 to 12 min with the rapid decreasing of catalyst particle size. It is possible that some Fe particles were etched off with further increasing duration of Fe film pretreatment. Consequently the distance among the particles increased greatly.

It is well known that the diameters and density of the catalyst particles controlled the growth of carbon nanotubes. Therefore, as the duration of catalyst pretreatment was increased from 6 to 12 min, the diameters of carbon nanotubes were decreased due to the decrease of the catalyst particle size. And the corresponding density of carbon nanotubes increased because of the increase of the density of the catalyst particles. On the other hand, the alignment of carbon nanotube arrays is attributed to the steric hindrance and van der Waals attraction among the carbon nanotubes during the growth process [28]. With the time of pretreatment increasing to 10 min, the steric hindrance and van der Waals attraction increased because of an increase in the density of the carbon nanotubes. Therefore, carbon nanotubes become straighter and have better alignment. However, although the density of the carbon nanotubes continuously increased after the pretreatment of the catalyst for 12 min in  $\text{NH}_3$ , the distance among them also increased because of etching effect. Accordingly the steric hindrance and van der Waals attraction among the carbon nanotubes decreased and consequently the formation of seriously curved carbon nanotubes.

The time of catalyst pretreatment not only affected the density and diameter of the carbon nanotubes but also the growth rate. With increasing duration of Fe film catalyst pretreatment in  $\text{NH}_3$  environment from 8 to 10 min, the growth rate of carbon nanotube increased and the amount of amorphous carbon particles and fibers decreased (as shown in Figs. 2 and 3). Furthermore, secondary growth of more carbon nanotubes took place, resulting in the increasing density of the carbon nanotubes in the top layer. However, with further increasing pretreatment duration to 12 min, the growth rate of carbon nanotube decreased greatly and amorphous carbon turned up again (as shown in Fig. 1).

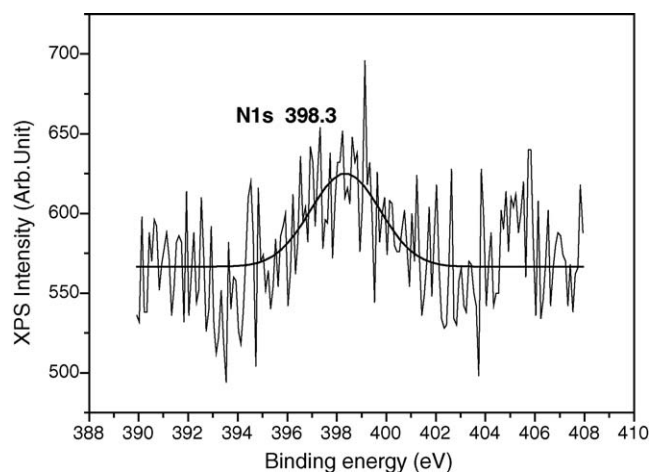


Fig. 6. The N 1s XPS spectra of catalyst Fe on Si wafer after pretreatment in  $\text{NH}_3$  for 8 min.

In order to clarify the effect of  $\text{NH}_3$  pretreatment on the growth of carbon nanotube arrays, we examined the N 1s XPS peak for Fe catalyst coated on silicon wafers after pretreatment (Fig. 6) in  $\text{NH}_3$ , which was fitted by a Gaussian line, with binding energy of  $398.1 \pm 0.2 \text{ eV}$ . From Fig. 6, active N atoms or related radicals decomposed from  $\text{NH}_3$  dissolved in catalyst particles after pretreatment for 8 min. Further analysis showed that the N/Fe atom ratio increased from 0.16 to 0.21 with the time of catalyst pretreatment increasing from 8 to 12 min (as shown in Table 1). The presence of active nitrogen in the catalyst during CNT growth can increase the activation of catalyst and enhance carbon diffusion into the catalyst [29]. Jung et al. [30] also proposed that the role of nitrogen would be either to enhance the formation of graphite layer on the catalyst surface or to increase the separation of the graphitic layers from the catalyst.

Table 1  
N/Fe atom ratio in the catalyst after pretreatment in  $\text{NH}_3$  for different time

Time of catalyst pretreatment (min)	Ratio of the N and Fe atoms
8	0.16
10	0.19
12	0.21

With increasing duration of pretreatment, the amount of active nitrogen, which came from the decomposition of  $\text{NH}_3$  might increase and lead to an increase in the amount of nitrogen implanted into the catalyst particles [31]. Therefore, the diffusion and precipitation rates of the carbon atoms increased and the chances of the aggregation of the carbon atoms into amorphous carbon decreased, resulting in an increase in the growth of the carbon nanotubes and a decrease of amorphous carbon. Moreover, the increase of the amount of the active nitrogen or related radicals might result in an increase of the density of nucleation sites on the surface of the catalyst particles [32], which might enhance the secondary growth of the carbon nanotubes. However, with further increasing duration of pretreatment in  $\text{NH}_3$  to 12 min, the amount of nitrogen implanted into the catalyst particles might increase greatly. Due to the strong binding force between active carbon and nitrogen atoms [33], excessive implanted active nitrogen interrupt diffusion of carbon atoms in the catalyst and their extrusion resulting in a decrease in the growth rate of carbon nanotubes. Consequently excessive carbon atoms congregated and formed amorphous carbon fibers or particles owing to successive carbon supply.

#### 4. Conclusions

In our experiment, the secondary growth of the carbon nanotubes occurred during the growth of carbon nanotube arrays after an appropriate pretreatment of Fe/Si catalyst in  $\text{NH}_3$  and layered carbon nanotube arrays were obtained. At the same time, the  $\text{NH}_3$  pretreatment exerts a great effect on the particle size and density of the Fe catalyst and its catalytic properties and hence the morphologies of the layered carbon nanotube arrays. Therefore, we can enhance the growth of carbon nanotube arrays by controlling the pretreatment of catalyst.

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