

# Novel selective process via self-assembled monolayers for pattern growth of carbon nanotubes

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## Abstract

In this study, a novel IC compatible deposition process to fabricate the CNTs pattern with tunable tube number density was successfully developed by using the liquid chemical technologies of self-assembled monolayers (SAMs) and the Fe-assisted CNTs growth. The tube number density could be controlled by changing the SAMs formation and post processing parameters. The Si wafers with the a:Si/Si<sub>3</sub>N<sub>4</sub> layer patterns were first prepared by low pressure chemical vapor deposition (LPCVD) and lithography techniques to act as the substrates for selective deposition of SAMs. The selectivity of SAMs from APTMS solution (*N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane) is based on its greater reactivity of head group on a:Si than Si<sub>3</sub>N<sub>4</sub> films. The areas of pattern with SAMs will first chelate the Fe<sup>3+</sup> ions by their diamine-terminated group. The Fe<sup>3+</sup> ions were then consolidated to become Fe-hydroxides in NaBH<sub>4</sub> solution to form the Fe-hydroxides pattern. Finally, the Fe-hydroxides pattern was pretreated in H plasma, and followed by CNTs deposition using Fe as catalyst in a microwave plasma-chemical vapor deposition (MPCVD) system to become the CNTs pattern. The products in each processing step, including SAMs, Fe-hydroxides and CNTs, were characterized by contact angle measurements, scanning electron microscopy (SEM), Raman, XPS and Auger spectroscopy. The results show that the main process parameters include the surface activation process and its atmosphere, consolidation time and temperature, H plasma pretreatment. The function of each processing step will be discussed.

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## 1. Introduction

Carbon nanotubes (CNTs) have attracted considerable interest since their first discovery by Iijima in 1991 [1]. The unique properties, such as chemical stabilities, mechanical, thermal, electric properties and high aspect ratio, which have subjected to the applications of chemical sensors [2], atomic force microscope/scanning tunnel microscope (AFM/STM) tips [3,4] and field emission display devices [5]. For the above applications, one of the key technologies is essentially to directly synthesize the CNTs on the well-defined areas with the required properties. In other words, the selective deposition processes have been devoted to synthesize the CNTs on the patterns with the pre-located catalysts [6–10]. Based on lithography techniques, traditionally the preparation methods of patterns with the pre-located

catalysts can be roughly divided into liquid- and gas-phase processes. The liquid-phase process is essentially a plating process, such as electroplating and electroless plating, and the gas-phase process is generally to deposit the catalyst by physical vapor deposition (PVD) or chemical vapor deposition (CVD) processes. In comparison with PVD or CVD processes, the liquid-phase process is in principle a low-cost process. It can also be used to deposit a large number of parts with the little limit in size, shape and orientation. For liquid-phase processes, pulse-current electrochemical method was proposed to grow the aligned CNTs with controlled site density, but the good uniformity in a larger area is limited by current distribution [11]. In this study, a modified liquid-phase process using self-assembled monolayers (SAMs) to deposit catalyst selectively onto the predefined a:Si pattern for CNTs growth with tunable tube number density was developed. The most important point of this novel process is its Si-based IC technology compatible feature.

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Table 1  
Specimen designation and processing conditions of CNTs

| Specimen designation | Surface activation conditions* | Consolidation time# (min) | Consolidation temperature# (°C) | H plasma pretreatment+ |
|----------------------|--------------------------------|---------------------------|---------------------------------|------------------------|
| A                    | Con. 1                         | 60                        | 25                              | 10                     |
| B                    | Con. 2                         | 60                        | 25                              | 10                     |
| C                    | Con. 3                         | 60                        | 25                              | 10                     |
| D                    | Con. 3                         | 20                        | 25                              | 10                     |
| E                    | Con. 3                         | 40                        | 25                              | 10                     |
| F                    | Con. 3                         | 60                        | 25                              | 10                     |
| G                    | Con. 3                         | 60                        | 80                              | 10                     |
| H                    | Con. 3                         | 60                        | 25                              | 0                      |

\* Where the pattern was dipped in 1 mM APTMS solution for 20 min, and then chelated in 1 mM Fe (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution for 5 min. Condition 1 (= anhydrous methanol cleaning + N<sub>2</sub> blowing), Condition 2 (= air baking) and Condition 3 (= Conditions 1 and 2).

# The Fe<sup>3+</sup>-chelated pattern was consolidated by 1 mM NaBH<sub>4</sub> solution for different consolidation times and temperatures.

+ The consolidated pattern was pretreated in H plasma (H<sub>2</sub> = 100 sccm, 9 Torr, microwave power = 200 W, substrate temperature approx. 550 °C) for 10 min, except specimen H, and followed by CNTs deposition in MPCVD system (CH<sub>4</sub>/H<sub>2</sub> = 1/100 sccm/sccm, 16 Torr, microwave power = 400 W, deposition time = 30 min, substrate temperature approx. 700 °C).

## 2. Experimental

In order to demonstrate the feasibility to synthesize a CNTs pattern, a comb-shaped pattern defined with amorphous silicon (a:Si) and Si<sub>3</sub>N<sub>4</sub> layers on the Si wafer was fabricated by means of I-line optical lithography and reactive ion etching (RIE) techniques. The pattern was then used as a substrate to study the selectivity of SAMs. The selectivity is based on the greater reactivity of surfactant head group of SAMs on a:Si than Si<sub>3</sub>N<sub>4</sub> films. Where the 100 nm thick Si<sub>3</sub>N<sub>4</sub> film was first deposited on Si wafer, and followed by 50 nm thick a:Si film by LPCVD method. To increase the packing density of SAMs, the a:Si surfaces were pre-activated by dipping in 2% HF solution and followed by boiling in 50% HNO<sub>3</sub> solution before SAMs deposition. Effect of additional surface activation on selectivity of a:Si with SAMs was further determined by adopting three different surface activation conditions, i.e. Condition 1 (= anhydrous methanol cleaning + N<sub>2</sub> blowing), Condition 2 (= air baking) and Condition 3 (= Conditions 1 and 2). The activated a:Si pattern was followed by a series of clean steps, and then immersed into 1 mM of anhydrous methanol solution of 1 mM APTMS for 20 min to form the SAMs pattern. Effect of preparation atmosphere (i.e. in N<sub>2</sub> and air) of SAMs on its wettability was also examined by measuring the contact angles between SAMs surface and de-ionized water as a function of deposition time. The SAMs pattern was then immersed in 1 mM Fe(NO<sub>3</sub>)<sub>3</sub> solution to chelate Fe<sup>3+</sup> ions on areas with SAMs to form the Fe<sup>3+</sup>-chelated pattern. The 1 mM NaBH<sub>4</sub> solution was then used to consolidate the Fe<sup>3+</sup> ions on the chelated pattern and followed by drying in air for different times and temperatures to form the Fe-hydroxides pattern. The Fe-hydroxides pattern was then reduced in 100 sccm H plasma at ~600 °C substrate temperature for 10 min

and followed by CNTs deposition in MPCVD system to form CNTs pattern. The processing conditions and specimen designations are shown in Table 1. Raman spectroscopy was used to examine the alkyl group of SAMs. The chemical status of SAMs and Fe-hydroxides patterns were examined by XPS and Auger spectroscopy. The carbon nanostructures were characterized by scanning electron microscopy (SEM).

## 3. Results and discussion

### 3.1. Substrate activation and processing atmosphere of SAMs

Regarding substrate activation, the results show that the packing density of SAMs on a:Si pattern can be enhanced by a series of activating processes, including HF dipping and HNO<sub>3</sub> boiling. Theoretically, the HF dipping step is essentially a SiO<sub>2</sub>-removal process on the a:Si and Si<sub>3</sub>N<sub>4</sub> areas to eliminate the possible interference. The HNO<sub>3</sub> boiling step is basically to react with Si to form Si-H bonding on a:Si and Si<sub>3</sub>N<sub>4</sub> surfaces to activate the surface. Furthermore, the results also indicate that the additional activation processes (Conditions 1, 2 or 3) can be manipulated to vary the selectivity of SAMs on a:Si substrates, as will be discussed in Section 3.4.

For processing atmosphere of SAMs, the contact angles between de-ionized water and SAMs formed for a series of deposition times and under N<sub>2</sub> or air atmospheres were compared, where SAMs were formed on the activated a:Si substrates by immersing in APTMS solution. It indicates that the contact angle of SAMs deposited under N<sub>2</sub> atmosphere has much less scattering with deposition time than under air atmosphere. It implies that the N<sub>2</sub> atmosphere can effectively block the moisture from atmosphere to react with APTMS, there-

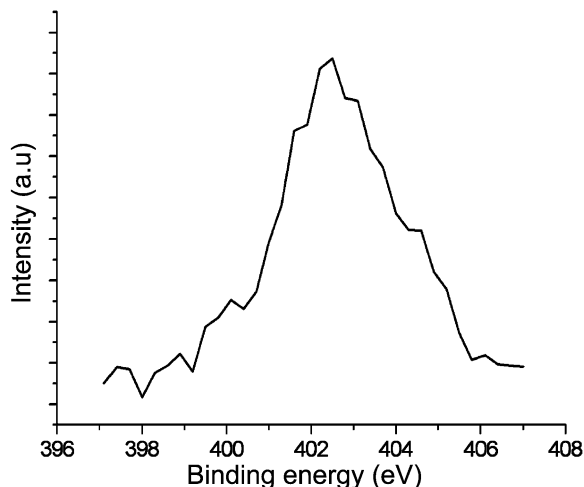


Fig. 1. The XPS spectrum of  $N_{1s}$  of as-deposited SAMs from APTMS solution on a:Si substrate.

fore, it results in a lower contact angle (approx.  $30^\circ$ ). Because the polymerization of APTMS with moisture will deposit on a:Si surface to occupy the areas with diamine-terminated SAMs, it results in a greater contact angle and lower wettability. In other words, atmosphere with lower moisture content is one of the key process factors.

### 3.2. Bonding characters of SAMs from APTMS

The XPS spectrum of SAMs deposited for 20 min under  $N_2$  atmosphere is shown in Fig. 1. Its peak value of  $N_{1s}$  at 402.5 eV is believed to be the chemical bonding of SAMs, because this peak is shifted approximately  $\sim 4$  eV from  $N_{1s}$  for  $NH_3$  ( $N_{1s}$ , 398.1 eV). An upper shift of  $N_{1s}$  in SAMs may be due to the fact that a greater ability of electron withdrawing of the terminal diamine group of SAMs. This is in agreement with the Raman spectrum for C–H bonding of SAMs on a:Si substrate (Fig. 2), where the  $\nu(C-H)$  stretching region of the SAMs at  $\sim 2850$ , 2894 and 2968  $cm^{-1}$  indicates existence of alkyl group of the SAMs on a:Si substrate.

### 3.3. Bonding characters and selectivity of Fe-hydroxides after consolidation

The XPS spectrum of the chelated and consolidated particles on a:Si substrate is revealed in Fig. 3. It indicates that the consolidated particles consist of iron, but are not in pure iron state, because its peak positions for  $Fe_{2p_{3/2}}$  and  $Fe_{2p_{1/2}}$  are  $\sim 713.0$  eV and  $\sim 727.5$  eV, instead of the corresponding literature values of  $\sim 707.0$  eV and 721 eV for pure iron, respectively. The particles are believed to be Fe-hydroxides due to high basicity (pH  $\sim 11$ ) of the  $NaBH_4$  solution after consolidation.

Effect of the a:Si substrates with additional surface

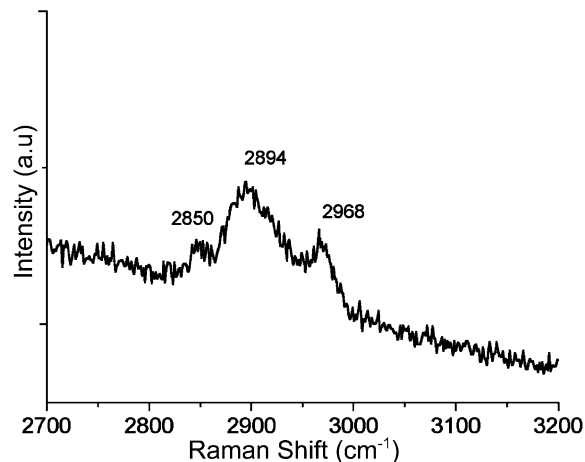


Fig. 2. The Raman spectrum of stretching region  $\nu(C-H)$  of the SAMs from APTMS solution on the a:Si substrate.

activation on selectivity of Fe-hydroxides was examined. The results show that Condition 3 (i.e. anhydrous methanol cleaning,  $N_2$  blowing and air baking) gives rise to a higher selectivity. Fig. 4a,b display the typical Auger spectra after consolidation for Condition 3 on the locations of pattern with  $Si_3N_4$  and a:Si as substrates, respectively. It reveals that there are no significant Fe signals in Fig. 4a, as compared with Fig. 4b, implying an excellent selectivity to Fe. In other words, Fe-hydroxides can be preferentially deposited on locations with a:Si as substrate, and the CNTs can be preferentially synthesized on locations with Fe-hydroxides as catalyst.

### 3.4. Selectivity of CNTs

The SEM morphologies of CNTs deposited on the consolidated patterns with three different additional surface activation processes (Conditions 1, 2 and 3) of a:Si substrates are shown in Fig. 5a, b and c with respect to

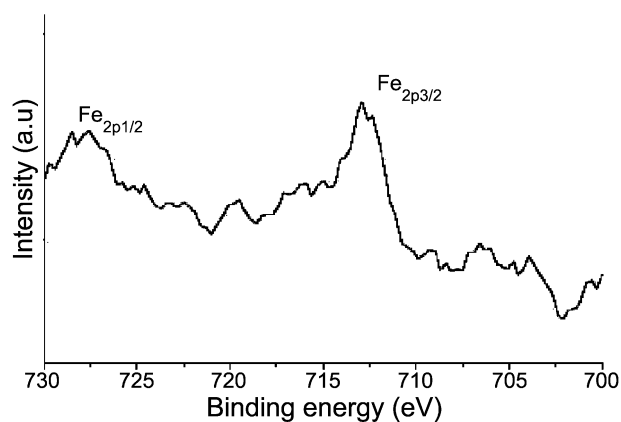


Fig. 3. The XPS spectrum of the Fe-hydroxides on SAMs after chelation and consolidation of  $Fe^{3+}$  ions on a:Si as substrate.

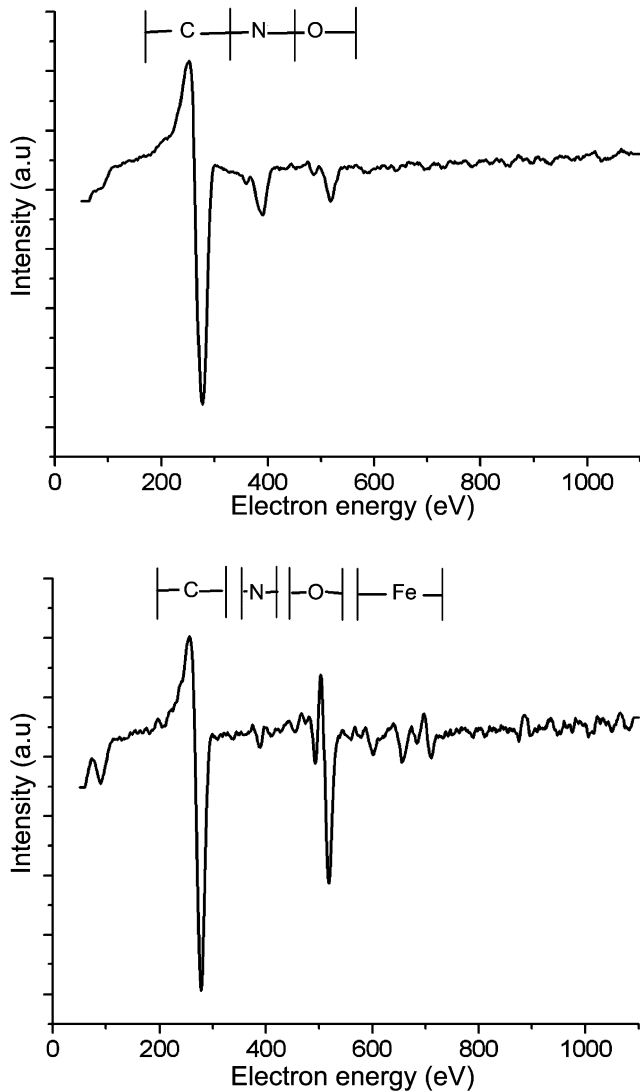


Fig. 4. The Auger spectra of the Fe-hydroxides on SAMs after chelation and consolidation of  $\text{Fe}^{3+}$  ions on the areas of: (a)  $\text{Si}_3\text{N}_4$ , (b) a:Si as substrates, respectively.

Specimens A, B and C, respectively. It indicates that the selectivity of CNTs is quite poor for Condition 1 (Fig. 5a), and is the best for Condition 3 (Fig. 5c). In other words, the four steps of surface activation before SAMs deposition is an important process step for a successful selective deposition of CNTs. The selectivity of this novel process is essentially based on the surfactant head group of APTMS molecules having higher reactivity with the substrate of a:Si than  $\text{Si}_3\text{N}_4$ . For the purposes of raising packing density and selectivity of SAMs on a:Si substrate, the a:Si patterns pre-activated by HF dipping and  $\text{HNO}_3$  boiling were followed by additional surface activation processing, including a combination of anhydrous methanol cleaning,  $\text{N}_2$  blowing and air baking. The procedure of anhydrous methanol cleaning plus  $\text{N}_2$  blowing is essentially to remove the possible

moisture and contaminants on the a:Si pattern, and to minimize oxidation of Si–H bonding from reacting with water and oxygen to maintain a:Si surface in activated state. The air baking step is basically to enhance the difference in reactivity between a:Si and  $\text{Si}_3\text{N}_4$  substrates. This is due to the fact that oxygen is more

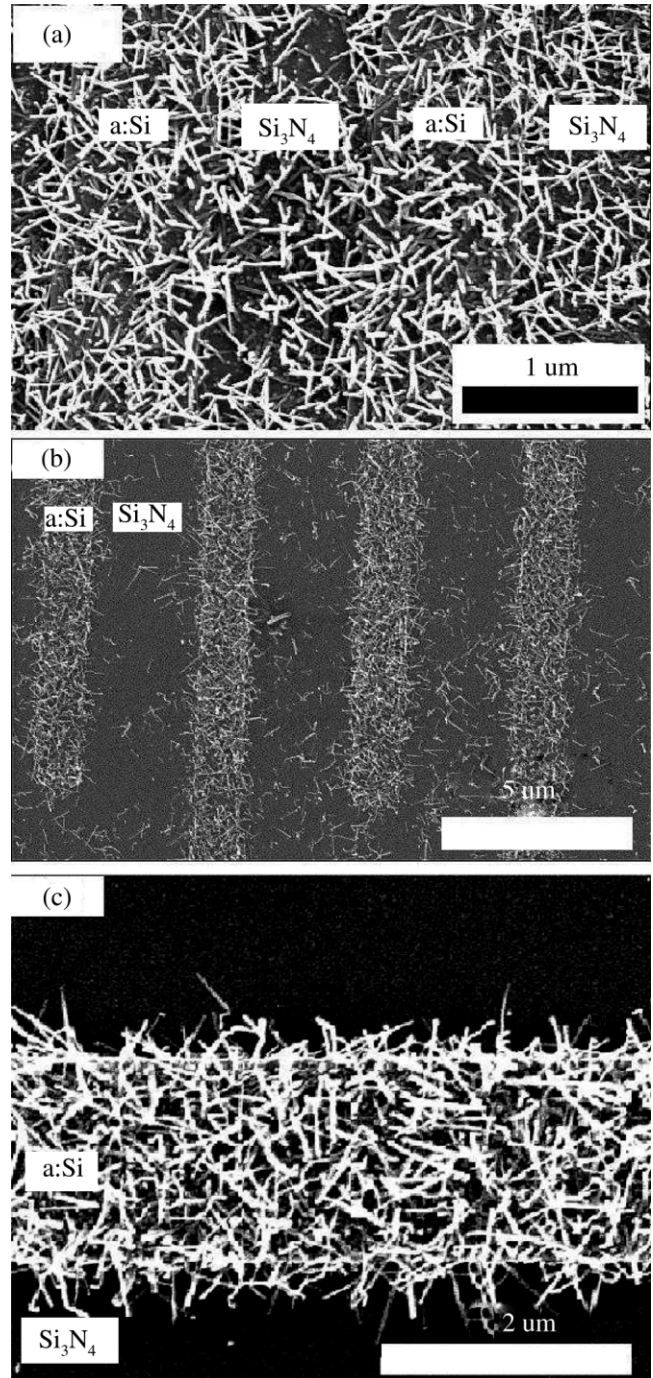


Fig. 5. The SEM morphologies of CNTs on the consolidated areas with a:Si as substrate pre-activated with different surface activation steps: (a) Con.1, (b) Con. 2 and (c) Con. 3, respectively, (Specimens A–C).

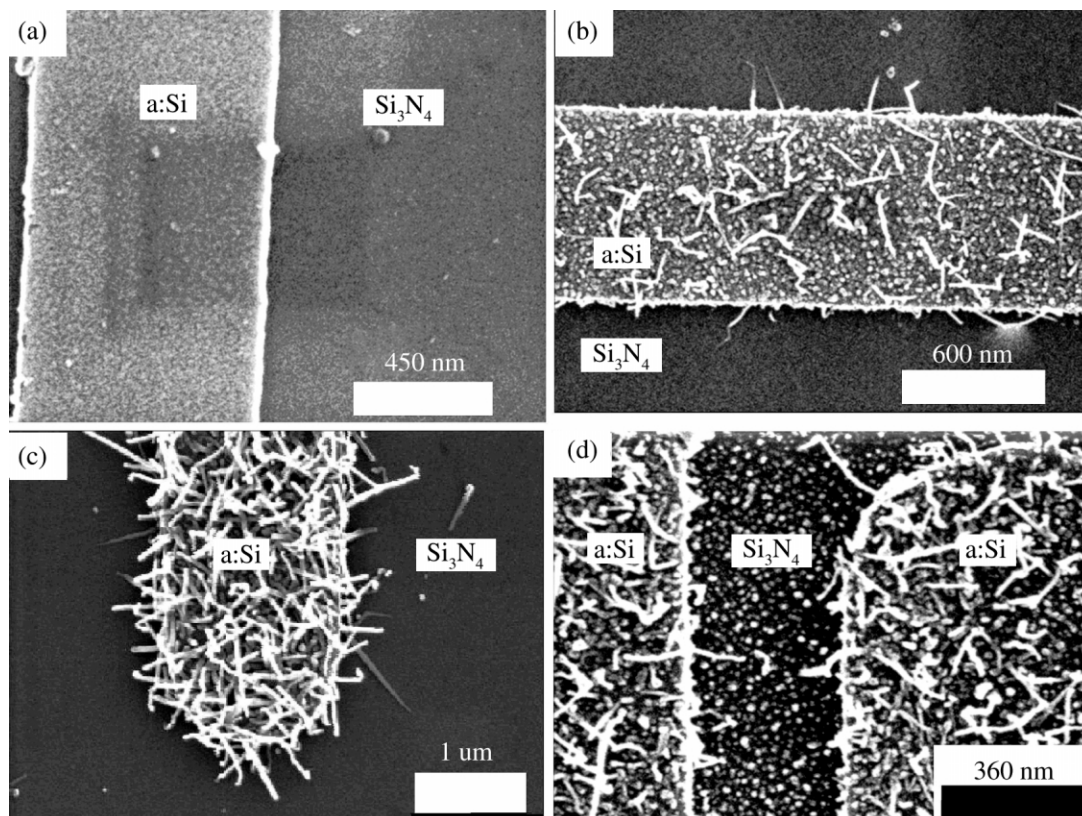


Fig. 6. The SEM morphologies of on the consolidated areas with a:Si as substrate pretreated with different consolidation times and temperatures: (a) 20 min, 25 °C; (b) 40 min, 25 °C; (c) 60 min, 25 °C and (d) 60 min, 80 °C, respectively, (Specimens D–G).

difficult to replace nitrogen in the denser  $\text{Si}_3\text{N}_4$  near surface to form  $\text{SiO}_2$  than a:Si. In other words, the Si–H bonding on  $\text{Si}_3\text{N}_4$  near surface will be removed much easier and become the original deactivated surface after air baking. On the contrary, the activated Si–H bonding on a:Si near surface will remain in the activated state after air baking, though it may be partially oxidized to become  $\text{SiO}_2$ , which has no significant effect on wettability of SAMs on a:Si substrate.

### 3.5. Effect of consolidation time and temperature on CNT growth

Fig. 6a–d display the SEM morphologies of CNTs on areas with a:Si and  $\text{Si}_3\text{N}_4$  as substrates under the same surface activation processes and H plasma pretreatment conditions for different consolidation times and temperatures, respectively (Specimens D–G in Table 1). It is obvious that there are no significant CNTs depositions on areas with  $\text{Si}_3\text{N}_4$  as substrate. By comparing the morphologies of CNTs on areas with a:Si as substrate for different consolidation times of 20–60 min (i.e. Fig. 6a, b and c, respectively), the tube number densities are in order of Fig. 6c > Fig. 6b > Fig. 6a. There are no significant differences in tube diameters. This can be reasoned by the fact that the consolidation time affects

the amount of  $\text{Fe}^{3+}$  ions to be consolidated and latterly to become catalyst for CNTs growth. It implies that the tube number density of CNTs can be effectively manipulated by varying the consolidation time. Effect of consolidation temperature on CNTs growth can be drawn by comparing morphologies of CNTs in Fig. 6c,d. It is believed that a higher consolidation temperature is basically to cause a higher reaction rate to consolidate more  $\text{Fe}^{3+}$  ions, therefore, more CNTs formation. However, a higher temperature would also result in more severe etching effect, especially under high basicity solution (pH ~ 11), to form a rougher surface on areas with  $\text{Si}_3\text{N}_4$  as substrates. This is in agreement with the great surface roughness in areas with  $\text{Si}_3\text{N}_4$  as substrate in Fig. 6d for 80 °C consolidation temperature.

### 3.6. Effect of H plasma pretreatment on CNT growth

The SEM morphologies of CNTs under the same processing conditions, except the patterns were processed with and without H plasma pretreatment, are shown in Fig. 6c and Fig. 7 (Specimens F and H in Table 1), respectively. It is obvious that the tube number density of CNTs for the specimen with H plasma pretreatment is higher. This is due to the fact that the effect H plasma pretreatment is essentially to reduce Fe-

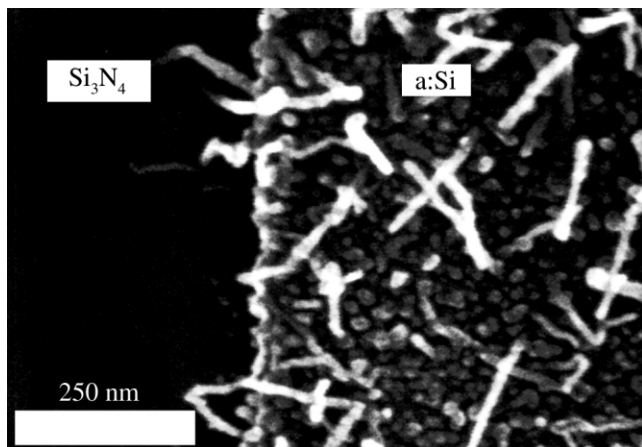


Fig. 7. The SEM morphologies of on the consolidated areas with a:Si as substrate with no H plasma pretreatment step (Specimen H).

hydroxides nano-film to become Fe nano-particles to act as catalyst for CNTs growth. For the pattern without H plasma pretreatment, the formation of Fe nano-particles and CNTs deposition occur simultaneously, so it results in a less tube number density of CNTs. Fig. 8a,b present the typical TEM microstructure and HRTEM lattice image of bamboo-like CNTs for Specimen F. They are tip-growth multi-walled CNTs with tube diameter  $\sim 128$  nm.

#### 4. Conclusions

A novel selective deposition process with IC compatible feature to fabricate the CNTs pattern with tunable

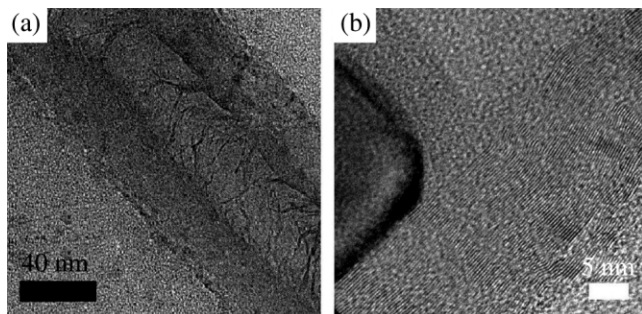


Fig. 8. (a) Microstructure (TEM) and (b) lattice image (HRTEM) of the typical bamboo-like CNTs, respectively, (Specimen F).

tube number density was successfully developed. The process is based on the difference in reactivity between a chosen couple substrates (a:Si and  $\text{Si}_3\text{N}_4$ ) with SAMs prepared from APTMS solution. From the experimental results, the following conclusions can be drawn: The main process parameters include the surface activation process and its atmosphere, consolidation time and temperature, H plasma pretreatment. For preparation of the SAMs pattern, surface activation processes through HF dipping,  $\text{HNO}_3$  boiling, anhydrous methanol cleaning,  $\text{N}_2$  blowing and air baking and under dry  $\text{N}_2$  atmosphere give rise to the best selectivity of SAMs between a:Si and  $\text{Si}_3\text{N}_4$ . The consolidation time and temperature can be adopted to manipulate the amount of Fe-hydroxides formation, therefore, to manipulate CNTs with different tube number density. However, a higher consolidation temperature may result in a greater surface roughness.

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