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Effects of ammonia on the alignment of carbon nanotubes in metal-assisted thermal chemical vapor deposition

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Abstract

The effects of ammonia on alignment of carbon nanotubes in an atmospheric pressure thermal chemical vapor deposition assisted by Ni were investigated. It was confirmed that ammonia is critical to the alignment of nanotubes at temperatures of 800–950°C. Both synthesis by C_2H_2 after ammonia pretreatment and synthesis by NH_3/C_2H_2 mixture flow could establish alignment. Alignment of carbon nanotubes due to ammonia was realized not by its influence on the morphology of the metal particles, but by its role of inhibiting a formation of amorphous carbon during the synthesis, particularly in its initial stage. © 2001 Published by Elsevier Science Ltd.

Keywords: Carbon; Films; Nanocomposites; Sensors

1. Introduction

The synthesis of aligned carbon nanotubes (CNTs) has been one of the important goals for their application to a tip material for the field-emission display. A few approaches have thus far been developed for this purpose. These methods include using catalytic metal particles with NH_3[1,2] and using catalytic-metal-embedded porous substrates.[3–5] For the first method, it was well agreed that the morphologies of the synthesized CNTs are intimately related with those of the catalytic metals. It was reported that metal particle sizes of several tens of nm are required for CNT synthesis with that method.[6,7] Ren at al.[1] reported that a catalytic role of NH_3 is necessary for CNT synthesis using plasma-enhanced hot filament chemical vapor deposition (CVD). Lee et al.,[2] however, claimed that NH_3 is critical to alignment of nanotubes, and furthermore, the role of ammonia is an etching of Ni particles to form an appropriate metal particle distribution. An additional process of HF etching was claimed to help the NH_3 etching process. Since it has been in controversy for the critical role of the NH_3 and no systematic investigations have been made, we report in this study a series of experiments to figure out the role of NH_3 in the morphologies of CNTs.

2. Experiment

Ni films of 10–40 nm were deposited on Si substrates using a dc magnetron sputtering method. The thickness of the thin films was estimated from the thickness of the films deposited measurably thick. The substrates with Ni films were placed in a 3″-diameter quartz tube furnace at room temperature and were pumped down to less than $\sim 10^{-3}$ torr using a mechanical pump. The substrate was then heated to a synthesis temperature with a rate of 20°C/min while introducing H_2 gas. Hydrogen gas reduces the oxidized surface of the Ni films. The synthesis temperatures were varied 600–950°C. When the temperature was stabilized, NH_3 gas was introduced, if necessary, with a flow rate of 60 sccm for 1 min while maintaining atmospheric pressure. C_2H_2 gas was then introduced with a flow rate of 30 sccm in atmospheric pressure for 20 min. Otherwise, mixtures of NH_3 and C_2H_2 gases in various ratios were introduced without NH_3 pretreatment process. The samples were then furnace-cooled slowly in a hydrogen flow ambient. The morphologies of catalytic Ni and synthesized CNTs were examined using a scanning electron microscope (SEM)

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and a high resolution tunneling electron microscopy (HRTEM).

3. Results and discussion

For systematic examination of the surface morphology of the Ni films and of the CNTs, a reference Ni film with a thickness of ~20 nm was chosen. The thickness was calibrated from thickness measurements on thick films, and thus should not be taken as an absolute value because the growth rate is not linear at the initial stage of the deposition. In this study, all the experiments were carried out on the reference samples unless otherwise specified. The metal morphology of a Ni film heat-treated at 800°C for 1 min is shown in Fig. 1a, which can be compared with that heat-treated at the same temperature while flowing NH_3 in Fig. 1b. When the metal films were heat-treated in the tube furnace for this purpose, amorphous carbon decoration of the metal particles, probably originating from the carboneous deposit on the quartz tube wall, were often observed. Therefore, the heat treatments were carried out in a new clean quartz tube to avoid possible carbon incorporation from the tube-wall, and are shown in Fig. 1. The Ni films coalesced to larger particles of uniform distribution, but the difference between the processes with and without the ammonia flowing is not noticeable. Namely the metal morphologies examined did not reveal definite clues to the role of the NH_3 in metal particles morphology.

However, the results of CNTs synthesis with and without the NH_3 pretreatment process were dramatically different. Fig. 2a shows the morphology of the CNTs synthesized by flowing C_2H_2 at 800°C without undergoing the NH_3 pretreatment process while Fig. 2b shows that with NH_3 pretreatment. Without NH_3 pretreatment, only such as shown curved or non-aligned CNTs were synthesized at all the temperatures between 700 and 950°C. Amorphous carbon was sometimes deposited and filled the space between the CNTs. On the contrary, very good alignment was realized with NH_3 pretreatments in the range of 800~950°C. Therefore, it is clear that ammonia pretreatment process is necessary to align the CNTs while the effect of the NH_3 pretreatment on the metal particle morphology for the alignment is unclear. Note that the method employed here is a very simple process. Other than the ammonia pretreatment process, such as HF dipping,[2] it is not necessary to align the CNTs.

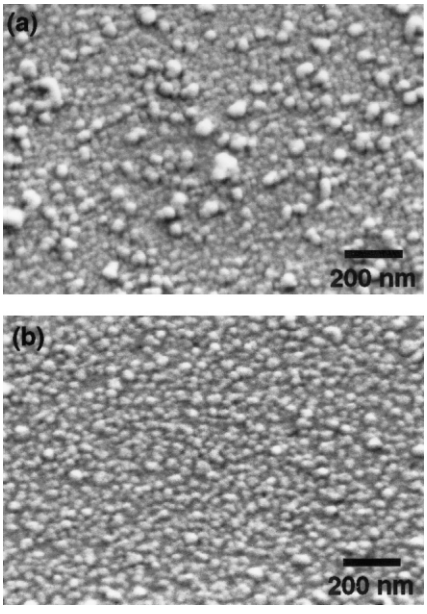

Fig. 1. Surface morphology of sputter-deposited 20 nm thick Ni films. Heat-treated at 800°C (a) without NH_3 and (b) with NH_3.

If the NH_3 pretreatment acts on the Ni films as an etching process, a prolonged etching will reduce the metal particle size as well as the particle distribution density. As a consequence, the synthesized CNTs on such films were expected to reveal thinner tubes with a less dense distribution. Although we extended the NH_3 pretreatment time till 60 min, however, still clear alignment with dense distribution was maintained (Fig. 2c). This result suggests that the role of NH_3 pretreatment is not an etching and may not be related to a formation of metal particle morphology. In the meantime, when we carried out a series of CNTs synthesis using mixtures of C_2H_2 and NH_3 gases in various mixing ratios without NH_3 pretreatment, good alignment was also established for $NH_3/C_2H_2 \geqslant 1$ (Fig. 2d). When $NH_3/C_2H_2 < 1$, curved CNTs were grown. This observation indicates that a prior NH_3 treatment is not necessary for alignment, and a critical amount of NH_3 during the synthesis is necessary for alignment of CNTs. The results thus far well coincide with the results by Ren et al.[1] in a plasma-enhanced hot filament CVD.

Now we need to figure out the reason for the alignment with the NH_3 pretreatment process. In the synthesis process of the NH_3 pretreatment and subsequent switching to C_2H_2 flow, we can easily assume a finite transition time for the refreshing of NH_3 by C_2H_2. In this initial stage of the synthesis, the remnant NH_3 after the switching may play a role for alignment. In order to test this possibility, we pumped out the ammonia after the pretreatment and refreshed the tube with H_2, and then C_2H_2 gas was introduced. The result was a curved CNTs growth. This experimental result clearly indicates that the role of ammonia in the alignment of CNTs is a catalytic role during the synthesis, particularly in the initial stage.

The detail mechanism of the catalytic role is not known at present, and should be further explored. However, one of the roles can be drawn from the following. When the synthesis time after the NH_3 pretreatment was varied, we found that the CNTs became thicker with time. This phenomenon was more remarkable at higher

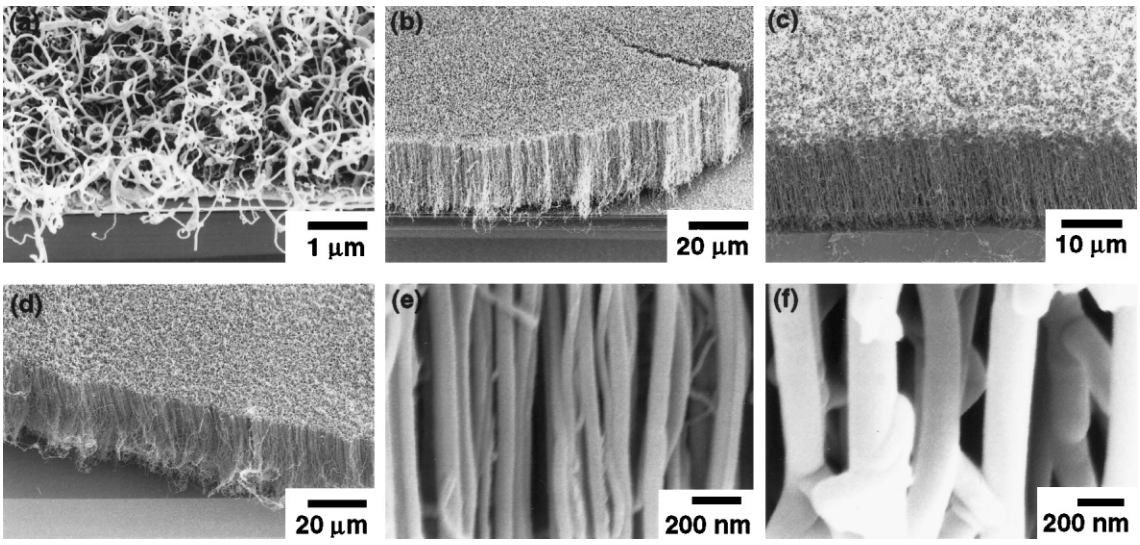

Fig. 2. Surface morphology of the CNTs synthesized on 20 nm thick Ni films. Synthesis at 800°C (a) without NH_3 pretreatment and (b) with NH_3 pretreatment for 1 min. (c) Synthesis at 850°C with NH_3 pretreatment for 60 min. (d) Synthesis at 850°C with C_2H_2:NH_3 = 30:30 sccm mixture flow without NH_3 pretreatment. Synthesis at 900°C on 50 nm thick Fe films with NH_3 pretreatment for 1 min for the synthesis time of (e) 20 min and (f) 60 min.

synthesis temperatures. Fig. 2e and 2f are the CNT morphologies grown at 900°C on 50 nm thick Fe films for 20 and 60 min, respectively, after 1 min of NH_3 pretreatment. A Similar trend was also observed for Ni films. It was revealed from a TEM observation that the thickening of CNTs was due to amorphous carbon deposit on the surface of the CNTs (Fig. 3) while the intrinsic features of the crystalline nanotubes in the wall thickness showed no difference with the synthesis time. It was also confirmed by a Raman spectroscopy measurement, although not shown here. We have to remark that there were no such amorphous carbon deposits until 1 h of the synthesis when a mixture of gases was used. It looks clear that NH_3 somehow prevents a formation of amorphous carbon from thermal cracking of acetylene in the furnace tube or in the metal particle. Recall that there was a tendency of amorphous carbon formation when synthesized without NH_3 pretreatment process.

This may be explained by an examination of the gas flow switching from NH_3 to C_2H_2. Since the switching is carried out in atmospheric pressure by opening-and-closing of the mass flow controllers, a transition in the gas partial pressures in the furnace is expected. Therefore, at the beginning of the synthesis, a partial pressure of the NH_3 residue is expected which will become thinner with time. The condition in the furnace tube in the initial stage of the synthesis with the NH_3 pretreatment is similar to that in the mixture flow for the synthesis. Ammonia, most probably, inhibits amorphous carbon generation in the initial stage of the synthesis, and thereby, protects the Ni metal particles from covered by amorphous carbon. With stopping of the role of NH_3 in the later stage of the growth, amorphous carbon begins to form and stick to the outer wall of the CNTs. Without ammonia, the initially synthesized amorphous carbons cover the metal particles and passivate their catalytic role resulting in curved random nanotube growth as well as the amorphous carbon deposition.

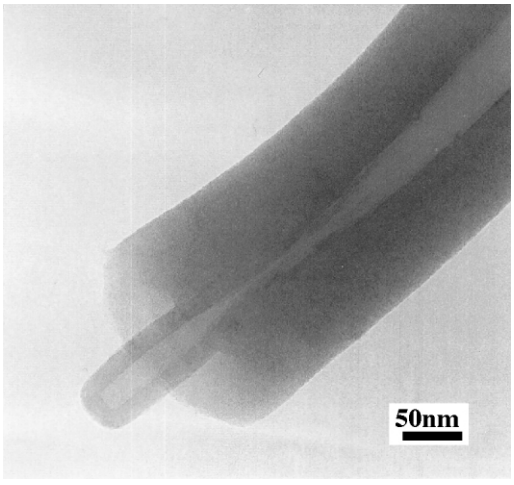

Fig. 3. TEM image of a carbon nanotube in Fig. 2f.

4. Conclusions

A series of experiments were carried out to investigate the role of ammonia in the synthesis of carbon nanotubes using atmospheric thermal CVD method. Ammonia was a critical element required to synthesize aligned CNTs. The alignment of CNTs both in the ammonia pretreatment process and in the gas-mixture flow process was consistently explained by the role of ammonia. The alignment due to ammonia was realized not by its

influence on the morphology of the metal particles, but by its role of inhibiting a formation of amorphous carbon during the synthesis.

Acknowledgements

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