

# A possible approach exploring the melting state of catalysts during the low-temperature growth of carbon nanotubes

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## Abstract

A method to qualitatively examine the physical state of catalysts has been demonstrated by simultaneously supplying Ti species for carbon nanotube (CNT) growth. Under a  $\text{TiCl}_4/\text{CH}_4/\text{H}_2/\text{N}_2$  plasma ambience, a continuous TiCN film was deposited on the Si substrate in the absence of catalysts; however, for the Ni-coated Si substrate, one-dimensional CNTs rather than TiC or TiCN nanofibers were grown through the catalytic vapor growth process, with the amorphous Ti-containing layers coated on their surfaces. The obtained coaxial CNT structure and the electron diffraction pattern analysis of catalysts support the factor that Ti atoms hardly dissolve into the catalyst and pass through it (or diffuse along the surface). Selective dissolution and diffusion between the Ti and C atoms in Ni nanoparticles suggest that catalysts during low-temperature growth of CNTs (580 °C) are not melted, instead they should be in solid state.

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## 1. Introduction

Carbon nanotubes (CNTs) have generated significant interest due to the outstanding properties as well as their potential applications for advanced devices. Several methods and numerous carbon-containing precursors have been employed to synthesize CNTs. Among these processes, catalytic chemical vapor deposition (CVD) [1] (i.e. with the assistance of catalytic nanoparticles) is the most promising technique for growing CNTs with well-defined growth characteristics (e.g. controllable length, diameter, packing density, position, and orientation) [2–5].

The vapor–liquid–solid (VLS) model [6] is the mostly proposed explanation for the growth of CNTs in CVD. This mechanism involves the formation of a metal–carbon liquid alloy at processing temperature above the eutectic point of the alloy. However, in the CVD deposition of CNTs, the growth temperature (about 500–900 °C) is usually far lower

than the melting point of catalysts or even the eutectic temperature of the alloy. The issue seems possible since the melting properties of nanoparticles would be corrected by the particle-size effect (high surface-to-volume ratio) [7] and the working pressure. Therefore, the theoretically higher processing temperature might not be essential. It is reported that the formation of eutectic compounds in catalysts is the common evidence for VLS mechanism [8]. On the other hand, some researches do propose that the solid state catalyst would be responsible for the CNT growth [9]. Referring to the synthesis of other one-dimensional (1-D) materials, there has been also suggested that the liquid intermediate is not a necessity and the solid state catalyst can also lead to the formation of these 1-D nanostructures [10]. To date, the exactly physical state of catalysts during CNT growth is still controversial because it is difficult to in situ monitor their characteristics. Though the synthesis temperature can be reduced while growing CNTs, whether the catalyst is in liquid state at a relatively low growth temperature (e.g. <600 °C) needs further examination, since there appears a large temperature difference to the eutectic temperature.

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In this report, we have made an attempt to qualitatively explore the melting characteristics of catalysts by simultaneously supplying  $\text{TiCl}_4$  in addition to hydrocarbon during vapor growth. The ultimate deposited products on both the bare Si and Ni-coated Si substrates provide the information accounting for the melting characteristics of the catalysts during CNT growth.

## 2. Experimental

The growth of CNTs was carried out by using a typical radio frequency (rf) PECVD process in a Pyrex bell-jar furnace. The reaction furnace was vertically set and connected to a rotary sliding-vane pump with a base pressure of 0.05 Torr. During the PECVD growth, the capacitively coupled plasma was generated between a set of internal parallel electrodes (separated by 5 cm), where the substrate was placed on the rf electrode with self-biasing. Two kinds of substrates were utilized. The bare Si (100) substrate was used for a blank experiment, while the Ni-coated one was used for the catalytic vapor growth. To obtain the catalytic nanoparticles as nucleation sites, Ni thin films were firstly treated by  $\text{H}_2$  plasma (100 W) at 580 °C for 20 min. Then, a gas mixture was introduced and the rf plasma was operated at 300 W to initiate the vapor growth. In addition to gases of  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{N}_2$  that are commonly used as precursors for CVD of CNTs, another reactant of  $\text{TiCl}_4$  vapor, carried by flowing  $\text{H}_2$  gas, was introduced simultaneously (the bubbler temperature was at room temperature). The working pressure was approximately 1–2 Torr and the deposition time was kept constant for 60 min.

The morphology of the as-deposited materials was observed using field emission scanning electron microscopy (SEM, Philips, XL-40FEG). For the deposits on blank Si substrate, the structure was determined by glancing incident angle X-ray diffraction (GIAXRD, Rigaku D/MAX2500) with a Cu  $\text{K}\alpha$  X-ray source and a fixed angle of 3.0°, and the composition was analyzed by energy dispersive spectrometer (EDS) equipped in SEM. As regards the products from catalytic growth, transmission electron microscopy (TEM, Hitachi, HF-2000 and JEOL, JEM-3010) at 200 and 300 kV was used to characterize the detailed structure of the individual 1-D material and the encapsulated catalyst, respectively. The composition distribution of the individual material was also characterized by EDS, which was equipped in TEM for a better spatial resolution.

## 3. Results and discussion

The Ni transition metal has been demonstrated as an efficient catalyst not only for the growth of CNTs but also for the synthesis of a variety of related carbide whiskers (e.g. SiC, TiC) simply via the addition of another metal element except carbon atom, where the VLS process is the well-

known mechanism for obtaining such high-aspect-ratio carbides. For instance, while growing TiC whiskers [11–13], the prerequisite in VLS process is the dissolution of Ti and C atoms into Ni particles and forms the Ni–Ti–C liquid droplets. Due to the similarity in preparation, an idea was initiated to explore the physical state of catalysts by deliberately supplying another species (Ti) to the precursors during CNT growth. Based on the phase diagrams, the eutectic temperature of Ni–Ti–C system is slightly lower than that of Ni–C (Ni–Ti–C: 1265~1295 °C, Ni–C: 1327 °C) [12], implying that the Ni–Ti–C liquid alloy could probably be obtained at a temperature below that required for forming the Ni–C liquid alloy. Therefore, if the formation of Ni–C liquid alloy (VLS) is the only route responsible for CNT growth, thermodynamically, it is also possible to grow TiC nanofibers under appropriate process control.

Fig. 1(a) shows the cross-sectional SEM image of the product on a blank substrate (i.e. in the absence of Ni catalysts) from a plasma ambience with additionally introduced  $\text{TiCl}_4$  vapor, where the flow rates of  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{H}_2$  (main gas), and  $\text{H}_2$  (carrier gas) were 18, 50, 100, and 100 sccm, respectively. In this case, a continuous film (~250 nm in thickness) was deposited on the bare Si substrate. Compositional analysis by EDS indicates that the coating is mainly composed of Ti, C, and N elements with atomic ratio of 48.17%:23.12%:28.71% (the ratio of Ti/

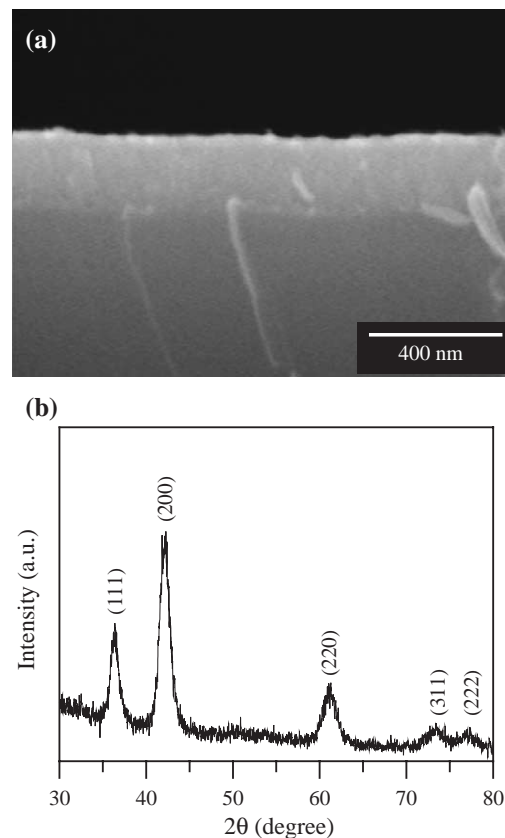


Fig. 1. (a) Cross-sectional SEM image of the as-deposited film on the bare Si substrate from a  $\text{TiCl}_4/\text{CH}_4/\text{H}_2/\text{N}_2$  plasma ambience. (b) GIAXRD spectrum of the as-deposited film in (a), showing the film with TiCn crystallites.

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