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Carbon nanotube formation directly on the surface of stainless steel materials by plasma-assisted chemical vapor deposition

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We have developed a method for forming carbon nanotubes (CNTs) directly on the surfaces of stainless steel materials that are important industrially. Using plasma-assisted chemical vapor deposition (PCVD), CNTs are formed at comparatively low temperatures, thus avoiding excessive annealing and degradation of the stainless steel. Because the catalytic metals needed for CNT formation are contained in the stainless steel materials themselves, coating processes of catalytic metals can be omitted. In the experiment, we prepared sample substrates made from stainless steel 304, which is representative of austenitic stainless steels. The PCVD was performed at 550~600°C by introducing methane gas to the substrates at a pressure of 260 Pa. The deposited samples were observed with SEM, TEM, and TEM-EDX. The results reveal that aligned multi-walled CNTs were formed directly on the sample substrates. The CNTs were typically ten layers and 15 nm in total diameter. To improve the uniformity of CNT growth across the substrate, we have tried a new pretreatment method in which the substrates are heated in the atmosphere before initiating PCVD.

Keywords: nano technology, new materials, processing plasma, film deposition, low temperature formation, pulsed glow plasma generation, MW-CNT, iron nanoparticles, metal alloy

1. Introduction

Recently, carbon nanotubes (CNTs), a new material expected as to be widely useful in many industrial applications, have been synthesized using various fabrication methods. Most of these employ chemical vapor deposition (CVD) processes in which raw gases including carbon are sprayed onto a heated substrate [1]. Typically, silicon (Si) wafers are used as substrates, and catalytic metal particles or thin films are precoated on the substrates prior to the CVD process. However, the necessity for such substrate materials and precoating processes tends to increase CNT production costs.

Metals have been used as primary materials for machine parts, structural elements, etc. in many industry fields. Much knowledge and techniques about them have also been accumulated. Forming CNTs on a metal substrate surface seems to offer great promise for industrial applications. In particular, stainless steel materials which have good workability, corrosion resistance, and potential for low cost, are desirable substrates. Although some studies of this subject have reported using thermal CVD processing methods [2,3], the prolonged high temperatures (> 700°C) required in such CNT formation processes produce significant annealing and degradation of stainless steel.

On the other hand, using plasma-assisted chemical vapor deposition (PCVD), CNTs can be grown at relatively low temperatures of less than 600°C [4]. Moreover, some stainless steel materials contain nickel (Ni) in addition to the primary alloy-constituent iron (Fe). If such metals contribute to CNT formation as catalyst, the precoating with catalytic metals can be omitted.

We have developed a CNT formation method using a PCVD process directly on the surface of substrates made from stainless steel. This article describes the CNT formation method that was developed and presents experimental results.

2. Experimental Setup

The configuration of the PCVD apparatus used for the CNT formation experiment is shown in Fig. 1. The apparatus consists of a high-voltage inverter power supply, a vacuum chamber, parallel-plate electrodes, a substrate heater, vacuum pumps, and a gas feeder. The parallel-plate electrodes are two circular plates, an upper and a lower one, made respectively of copper and molybdenum (Fig. 2(a)). A sample substrate is placed on the lower electrode, which has a substrate heater.

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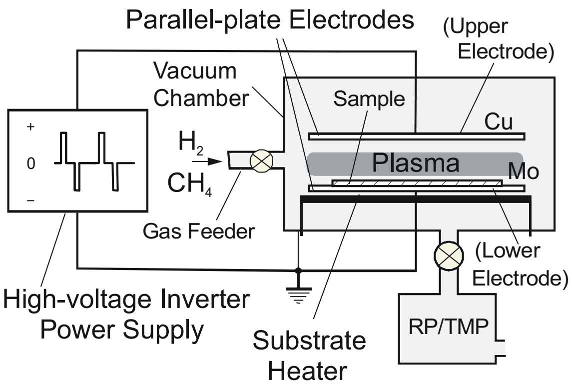
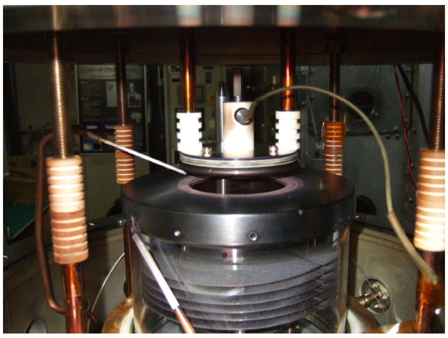
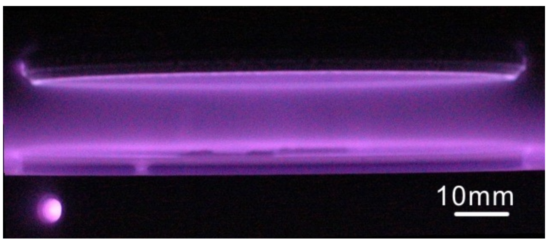


Fig.1 Schematic diagram of the PCVD apparatus for CNT formation. This system has been developed by ULVAC, Inc. and Osaka Univ.

After the vacuum chamber is exhausted by the rotary pump and the turbo molecular pump, raw material gases are introduced to the vacuum chamber. Mass flow controllers in the gas feed control the gas flow rate. The high-voltage inverter power supply is connected to the parallel-plate electrodes, and applies low-frequency bipolar voltage pulses to them [5]. In accordance with the applied pulses, a glow plasma is generated between the electrodes as shown in Fig.2(b), where the electrodes were surrounded by methane gas at about 260 Pa and subjected to exciting bipolar voltage pulses of 5kHz repeating frequency.



(a)



(b)

Fig.2 Photographs of the PCVD apparatus for CNT formation. (a) Parallel-plate electrodes and substrate heater (b) Light emission from the pulsed glow plasma (methane 260Pa, 5kHz)

This plasma generation method has the following characteristics. First, due to the low-frequency excitation, the structure of the power supply and the discharge electrodes can be simplified compared with those required for radio-frequency and microwave excitation. Second, good spatial uniformity of the plasma can be expected because the low-frequency wave does not produce a standing wave with fine structure or internal variations. These characteristics have advantages when treating large surface areas in the future. Third, the plasma parameters can be improved by increasing the pulsed current value. In the case of an argon gas plasma, the typical peak values of electron density and electron temperature are 6 x 10^{15} cm^{-3} and 7 eV, respectively [6].

As shown in Fig.1, the electrodes exposed to plasma, metallic species sputtered from the electrodes may affect the deposited film quality. However, the CNT growth itself is supposed not to be inhibited by the sputtered metallic species because both copper and molybdenum used for the electrodes are hardly to be carburized in contrast with the above catalytic metals.

3. Results and Discussion

A CNT formation experiment was carried out as follows. We used stainless steel 304 as the substrate representing austenitic stainless steels. The substrates were 20 x 20 mm squares cut from a commercial cold-rolled strip 1 mm thick, and cleaned in an ultrasonic washer with acetone. The sample substrate was placed on the lower electrode in the PCVD apparatus. When the sample temperature reached 550°C in vacuum, hydrogen gas was introduced into the vacuum chamber at 50 sccm and the plasma discharge was used to clean the substrate surface at a pressure of 1000 Pa for 20 minutes. Next, methane gas instead of hydrogen gas was introduced at 50 sccm. The plasma discharge was maintained for a further 60 minutes. The plasma was excited by rectangular pulses of +1kV/-1kV heights, 1.5 µs width, and 5 kHz frequency.

An FE-SEM image of the sample substrate after the PCVD process is shown in Fig.3. Some fibers were observed to be aligned almost perpendicularly to the substrate. A TEM image of such fibers is shown in Fig.4. It was found that the fibers were typically multiwalled carbon nanotubes (MWCNTs) with ten layers and a total diameter of 15 nm. It was also found that the CNTs had catalyst particles in their tips.

The results of the above experiment showed that MWCNTs were formed directly on the surface of stainless steel 304 substrates without requiring the precoating of any catalyst. However, the regions where CNT grew were limited to tiny areas as shown in Fig.3. Such CNT growth regions had a tendency to concentrate

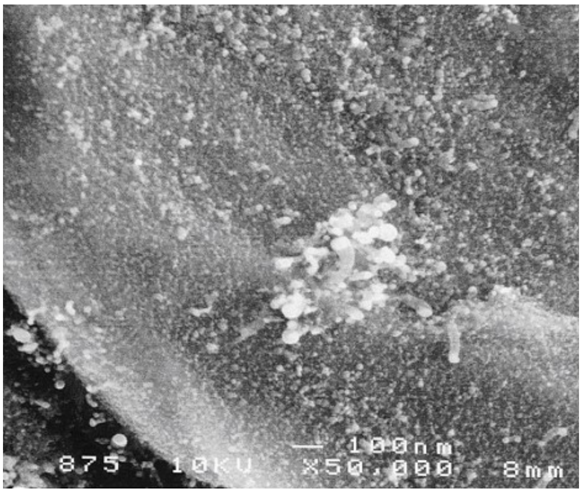


Fig.3 FE-SEM image of the surface of a sample stainless steel 304 substrate after the CNT formation PCVD process. A few fibers can be seen near the center of the image.

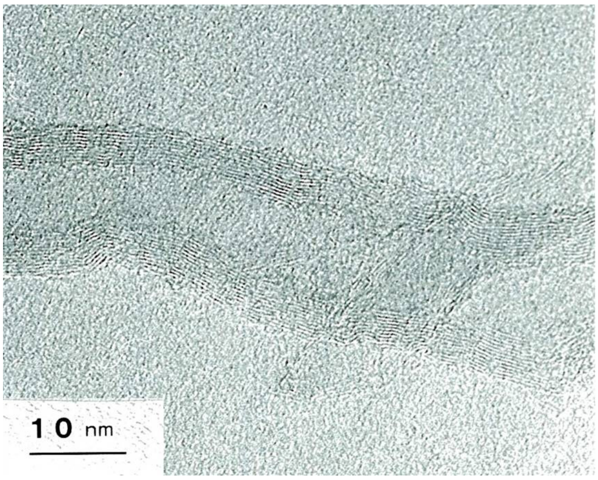
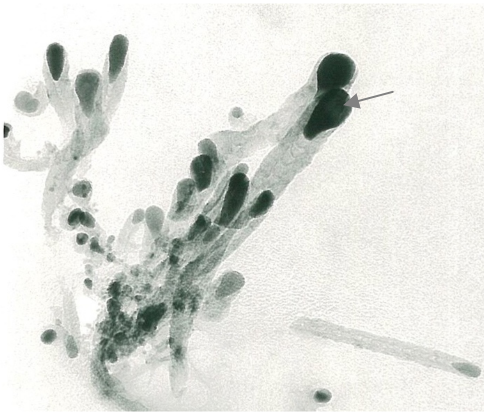


Fig.4 TEM image of the fibers shown in fig. 3.

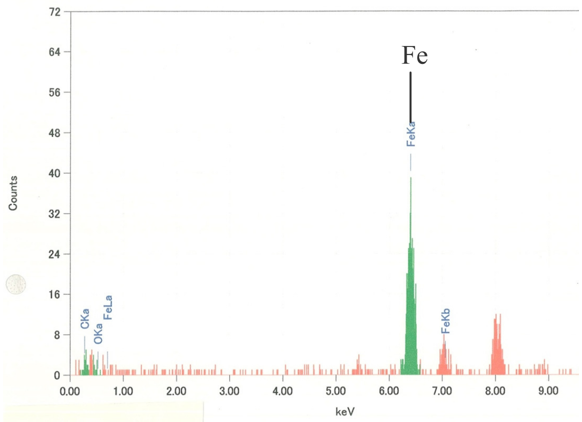
along scratches and marking indentations on the substrate. Hence, the CNT growth was considered to be notably sensitive to some condition of the substrate surface. To examine the cause, TEM-EDX was used for the material elemental analysis of the particles in the CNT tips. The results of the TEM-EDX analysis are shown in Fig.5. The particles were found to be almost exclusively Fe, although the Fe content of stainless steel 304 is about 70%. The other alloy constituents, Ni and Cr, were hardly included. It was estimated that some condition in the PCVD process made Fe alone act as a catalyst.

As is well known, stainless steel surfaces are covered with a chromium oxide thin layer. Thus, a shortage of Fe in the stainless steel surface layer might cause the non-uniformity of the CNT growth regions over the substrate surface. Accordingly, we devised a pretreatment method to supply more Fe component on the substrate surface, taking a hint from the formation of another oxide film when stainless steel materials are heated at a high temperature in the atmosphere [7, 8]. This oxide film can contain more Fe, which is thermally diffused from the stainless steels interior through the chromium oxide layer. In contrast, during the process of heating for the CNT formation, it is supposed that such iron-rich oxide films could hardly be grown because the substrates were heated in vacuum, that is, in a low partial pressure of oxygen [8].

As a test, we heated the substrate in the atmosphere at about 300°C for 20 minutes before the PCVD process. The appearance of the substrate just after the pretreatment is shown in Fig. 6(a). The sample substrate discolored to light brown from its original metallic luster. Next, the PCVD process was carried out on the pretreated substrate under the same conditions as the trial pictured in Fig.3. The FE-SEM image of the processed substrate is shown in Fig. 6(b). CNTs then grew uniformly over the substrate



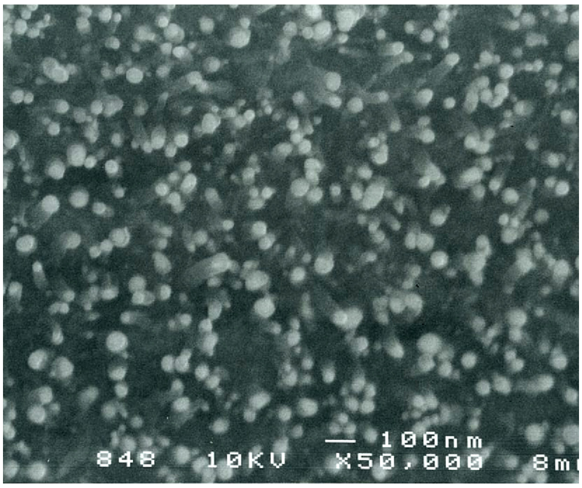
(a)



(b)

Fig.5 Results of TEM-EDX analysis of the particles included in CNTs
(a) TEM image of sample CNTs. The small arrow points the measurement area.
(b) Obtained X-ray energy spectrogram

(a)



(b)

Fig.6 Results of the CNT formation PCVD process for a pretreated sample substrate
(a) Stainless steel 304 sample substrate (20 x 20 mm) just after pretreatment. The letters on the substrate were marked for other purposes.
(b) SEM image of the pretreated substrate after the PCVD process with the same conditions as those for fig.3.

surface, showing that the pretreatment method was effective.

4. Conclusions

We have described a method for forming CNTs directly on stainless steel substrates using a PCVD process. The experimental results reveal that aligned MWCNTs were formed directly on a stainless steel 304 substrate. It was also observed that the CNTs included particles that were found to be composed primarily of Fe. Then we devised a new pretreatment method for the stainless steel substrate to improve the uniformity of the CNT growth. Further work is needed to optimize the conditions of the pretreatment and the CNT formation process. Applications of the developed method are currently being investigated.

5. References

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