



Article Growth of Carbon Nanotubes on Diamond with a Robust Structural Connection via Microwave Plasma Chemical Vapor Deposition

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Abstract: In this paper, we present a novel method for growing carbon nanotubes (CNTs) via microwave plasma chemical vapor deposition (MPCVD) on diamond and silicon substrates. Scanning electron microscopy (SEM) and Raman spectroscopy analyses revealed dense, multi-walled carbon nanotubes growing on the diamond substrate. Optical Emission Spectroscopy (OES) showed that in the process of growing carbon nanotubes with the MPCVD method, the CH₄ introduced into the system is excited by microwaves and dissociated to form active radicals such as C2 and CH, which are considered the C source of the synthesized carbon nanotube. Observation with high-resolution transmission electron microscopy (HRTEM) showed that most Ni catalyst nanoparticles that catalyze the growth of carbon nanotubes are located close to the diamond surface. In contrast, on the Si substrate, Ni catalyst nanoparticles were randomly distributed. A unique transition layer was observed between the diamond and carbon nanotubes, with the Ni particles being immersed into this transition layer and acting as anchors to fix the carbon nanotubes, resulting in a robust connection between the diamond and the CNT coating.

Keywords: carbon nanotubes; diamond substrate; microwave plasma chemical vapor deposition; catalyst nanoparticles; transition layer

1. Introduction

Numerous carbon-based materials have formed a huge and comprehensive system based on their diverse structures and unique properties. Therefore, carbon-based materials have been extensively studied and applied to many fields over the decades. Among them, carbon nanotubes (CNTs), one of the carbon allotropes, have become an attractive and interesting area since Iijima proposed and characterized them in 1991 [1]. Since then, their preparation methods, structural properties, and applications have been extensively studied [2,3]. In recent years, CNTs have shown significant potential in many application areas, such as electron field emission (EFE) materials [4], outgassing optical detection [5,6], and micro electromechanical systems (MEMS) [7]. These advances are attributed to the intrinsic properties of CNTs as well as their morphology, density, thickness, disorder, and tube size.

Many preparation methods for CNTs have been developed over the decades, such as arc discharge, flame synthesis, and chemical vapor deposition [8–10]. Chemical vapor deposition (CVD) has become the chosen method for large-scale production and synthesis of CNTs due to its simplicity, efficiency, and lower cost [11]. Thermal Chemical Vapor Deposition (TCVD) is a classic method for preparing carbon nanotubes [12]. However, the preparation of CNTs by TCVD usually requires an operational temperature higher than 800 °C, which excludes numerous substrates. For example, the growth temperature of CNT on various glass substrates for field-emission display must be lower than 500 °C [13]. Microwave plasma chemical vapor deposition (MPCVD) is one of the most popular methods



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). for the growth of many carbon materials, such as diamond film [14]. If MPCVD is used, the decomposition temperature of the carbon source can be significantly reduced, thereby reducing the substrate temperature and successfully growing CNTs at a low temperature.

It is now known that CNTs can grow on a variety of substrates [15], such as silicon and other Si-based compounds [16–18], quartz [19], alumina [20], zeolites [21], magnesium oxide [22,23], and NaCl [24]. However, most of these substrate materials have limited thermal conductivity and are significantly different in structure compared to the CNT. Furthermore, there are low adhesion forces between the CNTs and the CNT-coated substrates [25].

Diamond is another famous carbon allotrope and has been applied in many scientific and technological fields due to its remarkable properties, such as its high thermal conductivity, electrical resistivity, chemical inertness, and radiation resistance [26]. Diamond can also act as a CNT substrate in order to utilize it as an all-carbon-based composite material. Compared with other substrate materials for CNT growth, such as Si, quartz, and various metal-based materials, diamond is the most stable. Diamond and CNTs are both allotropes of carbon and are similar in many aspects. Since both diamond and CNTs have extremely high thermal conductivity, both diamond and CNTs can be combined, and the conversion efficiency between heat and light can be further improved, making it a promising material in the field of high-intensity endothermic or high-radiation black coatings or the field of chip cooling with excellent thermal interfaces and high conductivity substrates [27]. Moreover, the strong adhesion forces between the CNTs and the diamond substrate are formed as a result of the allotrope structure and intimate chemical properties, forming an effective chemical bond between the CNTs and the diamond. Therefore, the growth mechanism of CNTs on the surface of the diamond and the bonding mechanisms at the CNT-diamond interface are worthy of investigation.

There have been previous reports on the preparation of CNTs on diamond substrates. Daisuke Takagi [28] catalyzed the growth of CNTs using nanoscale diamond particles, Vavanasi [29] demonstrated that high-quality multi-wall CNTs can be grown on diamond substrate without using an intermediate oxide buffer layer, Varshney [30] developed a simple method to make diamond-CNT composite films by using candle wax as a precursor, without any metal catalyst, and Jiang [31] fabricated diamond/Ni/graphite/CNT composite films and evaluated their field electron emission properties, which showed a low turn-on field of 6.9 V/ μ m and good current stability. These works lay the foundation for the fabrication and application of CNT/diamond composite materials. However, the growth characteristics of CNTs on diamond substrates as well as the bonding mechanisms between the two still lack in-depth research and characterization.

Herein, we synthesized CNTs on a self-standing diamond film (and Si) via the microwave plasma chemical vapor deposition (MPCVD) method and fabricated a "CNTdiamond" full-carbon structure. This study demonstrated the possibility of the growth of a high-density CNT coating on diamond with excellent adhesion forces. It can be inferred that the strong bonding between the CNTs and the diamond substrate is attributed to the formation of a transition carbon layer at their interface during the reaction.

2. Experimental

2.1. Preparation of Substrates

In this study, diamond and Si smooth wafers were chosen as the carbon nanotube growth substrates. First, a 3-inch(7.65 cm) self-standing CVD diamond plate was prepared using the Direct Current Arc Plasma Jet CVD method (Figure 1a). Next, it was flattened with an automatic polishing and grinding machine (UNIPOL-802A) in order to make the average surface roughness (Ra) of the polished diamond substrate less than 10 nm (Figure 1b,c), which is similar to that of the Si substrate. Finally, the CVD diamond plate was cut into $10 \times 8 \times 0.5$ (mm) sections and used as the substrate for CNT growth. The same-size Si substrates were also used for comparative experiments.



Figure 1. (**a**) Schematic diagram of diamond thin film synthesis; (**b**) polished diamond image; and (**c**) the AFM image of its surface.

A high-vacuum multi-target magnetron sputtering (GCP-500M2) coating system was used to coat the substrate with a Ni layer approximately 10 nm thick. Ni sputtering was carried out at 200 °C for 120 s with a sputtering power of 70 W and chamber pressure held constant at 0.5 Pa. More details regarding Ni deposition are shown in Table 1.

| Table 1. Ni ca | atalytic layer | deposition [•] | parameters. |
|----------------|----------------|-------------------------|-------------|
|----------------|----------------|-------------------------|-------------|

| Target | Sample | Sputtering | Sputtering | Cavity | Bias | |
|----------|---------------|------------|------------|-------------|-----------|--|
| Material | Temperature/° | C Power/W | Time/min | Pressure/Pa | Voltage/V | |
| Ni | 200 | 70 | 2 | 0.5 | 100 | |

2.2. Synthesis of Carbon Nanotubes

CNTs were prepared via a microwave plasma chemical vapor deposition (MPCVD) method on diamond and Si substrates. In the experiment, the diamond substrate with the Ni coating was in a pure H₂ atmosphere in order to carry out the catalyst thermal annealing process, converting the Ni catalytic layer into Ni nanoparticles.

As shown in Figure 2a,b the annealed Ni particles on the diamond substrate are uniformly distributed with no apparent agglomeration or dispersion, indicating that there is no significant mutual dissolution between Ni and C at this temperature. The average particle density reached approximately 7000 (per μ m²). As shown in Figure 2c,d, after annealing, Ni nanoparticles were also formed on the silicon substrate; however, the overall particle density was smaller than that of the diamond surface, with an average particle density of about 5000 (per μ m²). During the thermal annealing process, the surface temperature of the sample was 550 °C, and the annealing time was 5 min. Details about the annealing procedure are shown in Table 2. CH₄, mixed with H₂, was used as a carbon source and passed through the MPCVD system at a ratio of 1:9. The CNTs were grown

using microwave energy to excite the carbon source gas, generating carbon-active radicals. During the carbon nanotube growth stage, the sample surface temperature was 600 $^{\circ}$ C, the corresponding microwave system output power was 1100 W, and the chamber pressure was 3.0 kPa. More details are shown in Table 3.



Figure 2. (a) SEM image of Ni nanoparticles formed on the diamond surface after annealing; (b) EDS elemental analysis image of Ni particles on diamond; (c) SEM image of Ni nanoparticles formed on a Si surface after annealing; and (d) EDS elemental analysis image of Ni particles on a Si surface.

| Table 2. Catalytic la | ayer annealing parameters. |
|------------------------------|----------------------------|
|------------------------------|----------------------------|

| Annealing Temperature/°C | Annealing Time/min | Microwave Power/W | Cavity Pressure/kPa |
|-----------------------------|--------------------|-------------------|---------------------|
| 550 | 5 | 1000 | 2.7 |

Table 3. Carbon nanotube growth parameters.

| Growth | Growth | Microwave | Cavity | CH ₄ :H ₂ |
|----------------|----------|-----------|--------------|---------------------------------|
| Temperature/°C | Time/min | Power/W | Pressure/kPa | |
| 600 | 30 | 1100 | 3.0 | 1:9 |

2.3. Characterization

The macroscopic optical characteristics of the pristine diamond substrates and CNTs were characterized via optical microscopy (OLYMPUS BX51, OLYMPUS, Japan) and the microscopic morphologies of the diamond substrates and CNTs were characterized by field emission environmental scanning electron microscopy (Zeiss GeminiSEM 300, Zeiss, UK). The interface samples of the CNTs and the substrates were prepared via focused ion beam (FIB) technology (Helios Nanolab 600i, FEI, USA). High-resolution images of single CNTs, CNT layers, and diamond substrates were obtained by transmission electron microscopy (JEM-2100F, JEOL, Japan; Titan ETEM Themis, FEI, USA). A high-spectral-resolution analytical-grade Raman imaging system (inVia-Qontor, Virsa, USA) was used to characterize the structure of the CNTs. The Raman laser model we used in the test has a

wavelength of 532 nm, the laser output power is 100 mW, the optical efficiency is 40%, the integration time is 30 s, and the magnification is 400 times. Detection of reactive radicals within the microwave plasma during nanotube growth was achieved via Optical Emission Spectroscopy (Ultim MAX, Oxford, UK). The adhesion force between the CNTs and the substrates was evaluated using ultrasonication and nanoscratch techniques (Hysitron TI 950, Hysitron, USA). For nanoscratch, a normal load of 500 μ N was used for all the scratch tests, and the length of each scratch was kept constant at 100 μ m.

3. Results and Discussion

During the growth process of the CNTs, the carbon source was decomposed on the surface of the catalyst, and the formed carbon atoms were dissolved into the catalyst, diffused, precipitated, and restructured in the catalyst particles, which is crucial to the structure and properties of the CNTs [32]. In this study, the carbon source constituting the CNTs primarily comes from the C-active radicals generated by the dissociation of CH₄. The growth temperature of the CNTs was 600 °C, while the pyrolysis temperature of methane was higher than 1000 °C [33]. Therefore, methane pyrolysis is negligible under the temperature conditions of this experiment. However, under microwave plasma, CH₄ molecules can be cleaved to form active C radicals at relatively low temperatures.

As shown in Figure 3a, the presence of carbon-containing reactive radicals such as C_2 and CH are generated by the decomposition of CH₄ and can be detected by OES spectroscopic diagnosis of the plasma during the reaction. These carbon radicals diffuse to the surface of the diamond substrate, collide with the Ni catalyst particles, and dissolve. When carbon saturation is achieved, the C atoms are precipitated from the catalyst surface and rearranged to form CNT structures [34]. Figure 3c presents a model diagram of the reaction process for producing CNTs using the MPCVD method. In the experiment, the sample with a Ni catalyst coating was placed upside down to reduce the strong bombardment of plasma and minimize its impact on the substrate and Ni catalyst, as well as CNT destruction.



Figure 3. (**a**,**b**) Optical emission spectra during CNT growth; (**c**) growth model of CNTs prepared by MPCVD and OES spectrum during the reaction process.

Figure 4a,b are the optical images of the diamond substrate before and after CNT growth. It can be seen that the CNTs are optically pure black. In the structure of the nanotubes, the chemical bonds between carbon atoms are mainly sp^2 hybrid bonds. Due to their optical transition characteristics of the π -bonds [35], the CNTs have strong optical absorption properties and appear pure black. Raman spectroscopy is a common means of detecting the structure of CNTs [36]. The Raman spectra of the pristine diamond substrate and the CNTs prepared on the diamond substrate are shown in Figure 4c,d. For the CNTs, the most prominent feature in its Raman spectra is the presence of an E_{2g} mode near 1580 cm^{-1} , which is the G-band. Additionally, there is a D-band near 1350 cm^{-1} , which represents a variety of possible defects. For multi-walled CNTs, the existence of a secondorder Raman spectrum between 2500 and 2900 cm⁻¹, is the G' band, also known as the 2D peak. Herein, the D-band signal represents the disordered sp³-hybridized carbon atoms and lattice voids existing in the hexagonal framework of the CNTs, while the G-band signal represents the graphitized arrangement of the sp²-hybridized carbon atoms in the CNT structure. Furthermore, the lower the intensity ratio of the D peak to the G peak (I_D/I_G), the greater the structural integrity of the CNTs. Figure 4e, f are SEM images of the diamond substrate and the CNTs. It can be observed that dense CNTs have grown on the diamond substrate after the MPCVD reaction, and those CNTs are intertwined with each other, which may be due to attraction via van der Waals forces.



Figure 4. Carbon nanotube samples prepared on diamond substrates: (**a**) optical microscope image of the original diamond substrate; (**b**) optical microscope image of carbon nanotubes grown on the diamond substrate; (**c**) Raman spectrum of the diamond substrate; (**d**) Raman spectrum of carbon nanotubes; (**e**) SEM image of the pristine diamond substrate; and (**f**) SEM image of carbon nanotubes.

Common substrate materials for CNT growth include Si, quartz, and MgO. In terms of material composition and molecular atomic structure, these substrate materials are fundamentally distinct from CNT materials. In this study, the diamond substrate and CNTs are both carbon substances that are allotropes, differing in the arrangement of atoms, and, thus, have great homogeneity. The bonding method between carbon atoms in diamond is a sp³-type hybrid bond, while in the tubular hollow structure of CNTs, the bonding method between carbon atoms is a sp²-type hybrid bond. In 2007, Suguru Noda [37] showed

that for the preparation of CNTs, different substrate materials may have different effects on the agglomeration and diffusion of catalyst particles and their final position, which ultimately affects CNT production. Other studies have mentioned that the interactions between CNTs and their substrates will affect the degree of separation between the CNTs and the substrates, which is also called the strength of the adhesion force to the substrate material [38].

Ultrasonication is a commonly used method for the measurement of adhesion between the CNTs and the substrate materials [39–41]. This method is used to reflect the strength of the adhesion between CNTs and the substrate materials by observing the detachment of CNTs under strong vibration. In this current study, we used the same method and process parameters to prepare CNTs on diamond and Si substrates. These samples were subjected to ultrasonic vibration in order to evaluate the bonding strength of CNTs to their respective substrates. The vibration duration was 24 h. After shaking, the detachment degree of the CNTs on the two substrates was compared. As shown in Figure 5a,b, after 24 h of ultrasonic vibration, the CNTs on the diamond substrate were only slightly detached, and most of the black CNTs remained attached to the diamond substrate. However, as shown in Figure 5c,d, nearly all the black CNTs on the surface of the Si substrate were detached, and most of the substrate was exposed. This comparison demonstrates that the adhesion force between the CNTs and the diamond substrate is much stronger. SEM images of the CNTs on diamond and Si substrates after ultrasonic vibration are shown in Figure 5e,f. It can be seen that the detachment of CNTs on the diamond substrate is much smaller than on the Si substrate.



Figure 5. Carbon nanotubes prepared on diamond and Si substrates: Comparison of CNTs on a diamond substrate (**a**) before and (**b**) after ultrasonic vibration; comparison of CNTs on Si substrates (**c**) before and (**d**) after ultrasonic vibration; (**e**) SEM image of CNTs on diamond after ultrasonication; and (**f**) SEM image of CNTs on silicon after ultrasonication.

A nanoscratch test is a method that can accurately quantify the adhesion force between the materials and the substrates. This method has also been applied to test the adhesion force between CNTs and their substrate material [42]. As shown in Figure 6, when the indenter tip swipes across the CNT sample surface with a constant normal load (500 μ N), CNTs are pulled from the substrate, at which point the indenter tip is subjected to an additional opposing force, which can be reflected by an increase in the detected lateral force. As shown in Figure 6a,b, there is a tendency for the lateral force detected by the indenter to increase. From the comparison shown in Figure 6c, it can be seen that the bonding force between the CNT and diamond is much greater than that with the Si substrate. This is in good agreement with the results of the ultrasonic vibration test described above. Considering that the difference between the Si substrate and the diamond substrate may affect the nanoscratch test results, we performed scratch tests on the original Si and diamond substrates, respectively. As also shown in Figure 6a,b, the lateral force did not change significantly when the indenter swiped across the diamond and Si substrates. Therefore, when diamond is used as the substrate, strong bonding with CNTs can be achieved.



Figure 6. Nanoscratch through the CNTs on Si and diamond substrates. Lateral force response during the nanoscratch tests on (a) CNT-diamond and (b) CNT-Si samples. (c) Comparison of lateral force increments for CNT-diamond and CNT-Si samples.

Based on the different adhesion forces of CNTs with Si and diamond, we first characterized and analyzed the morphology and structure of the CNTs fabricated on these two substrates. Figure 7a,b are SEM images of the morphologies of CNTs prepared on diamond and Si substrates. Both groups of CNT samples appear as interwoven networks. We also analyzed the difference in the Raman characteristic peaks of CNTs prepared on Si and diamond, as shown in Figure 7c. The I_D/I_G value in the Raman spectrum of the prepared CNTs is slightly smaller than that of the CNTs grown on Si, indicating that the CNTs prepared on the diamond substrate have relatively few defects. Therefore, a well-structured CNT structure is grown on the diamond substrate, which may be one of the reasons why the bonding force between the CNTs and diamond is greater than that with a Si substrate. Figure 7d,e are HRTEM images of CNTs prepared on diamond and Si substrates. It can be seen that both are multi-walled CNTs, and their structure is nearly the same. There are approximately 10 walls within the CNTs, and the diameter of the tube is approximately 15 nm.



Figure 7. Comparison of carbon nanotubes grown on diamond and silicon: (**a**) SEM image of CNTs on diamond; (**b**) SEM image of CNTs on silicon; (**c**) Raman pattern of carbon nanotubes on silicon and diamond; (**d**) HRTEM image of carbon nanotubes grown on a diamond substrate; and (**e**) HRTEM image of carbon nanotubes grown on a silicon substrate.

To further explore the reasons for the difference in the adhesion of CNTs on diamond and silicon substrates, we analyzed the structures of the bonding interfaces of CNT-Si and CNT-diamond, respectively. Figure 8a is a cross-sectional SEM image of the diamond substrate with CNTs. It can be observed that the height of the CNT sample is approximately 0.9–1 µm. Figure 8b–d are TEM images near the CNTs-diamond interface. In Figure 8b, the left and right sides are CNTs and the diamond, respectively, and the numerous spherical particles on the CNT side near the interface are Ni particles. As shown in Figure 8c, the tube wall structure of CNTs can be distinguished in the high-resolution image near the Ni particles, confirming that during the MPCVD reaction, the Ni particles successfully catalyzed the growth of the CNTs. Figure 8d is the HRTEM image of the interface between diamond and CNTs, which shows the layer-by-layer CNT tube wall structure around the Ni particles. Figure 8d also reveals a transition graphite region with a thickness of about 6 nm between the diamond substrate and the CNTs. The formation of this transition layer is considered to be the product of the mutual reaction between Ni and the diamond substrate. The carbon atoms in the diamond diffuse into the nickel particles during the re-action; the out-diffusion process invariably generates structural defects, resulting in the formation of the graphite layer [43]. The Ni particles are immersed in this transition layer and act as anchors to fix the CNTs, resulting in a robust connection between the diamond and the CNT coating.



Figure 8. The structure of the CNT-diamond interface: (a) SEM image of the CNT-diamond interface; (b) TEM image of the CNT-diamond cross-section; (c) TEM image of Ni particles and surrounding CNTs; and (d) TEM image of the CNT-diamond interface.

Figure 9 provides an image of the morphology and structure of the CNTs-Si interface, and Figure 9a is the SEM image of the CNT-Si interface, showing the thickness of the CNT layer is approximately 1 µm. Figure 9b shows the TEM image of the CNT-Si interface. It is observed that the Ni particles are relatively uniformly dispersed throughout the CNT sample area, which is significantly different from the distribution characteristics of Ni particles at the CNT-diamond interface (Figure 8b). This indicates that most of the Ni particles are not effectively anchored onto the surface of the Si substrate compared to the diamond substrate. As shown in Figure 9c, the tube wall structure of the CNTs can also be observed around the Ni particles, verifying that the CNT structures grow around the Ni particles. Figure 9d is a HRTEM image of the CNT-Si interface. The CNT sample is almost directly on the Si interface, and there is little "transition layer" on the Si substrate, which is in contrast to CNT growth on the diamond substrate (Figure 8d).

We conducted additional research on the robust binding force between CNTs and diamond, as well as the special structural features at the CNT-diamond interface, using HRTEM characterization. We performed an EDS line scan analysis along the upward growth direction of the CNTs (relative to the diamond substrate). As shown in Figure 10a,b, the direction of EDS detection is shown by the green line segment, starting from the diamond substrate and measuring along the radial growth direction of the CNTs. It was found that the content of Ni is largely near the root of the CNT, indicating that the catalyst Ni particles are located throughout the bottom of the CNT during and after the growth of the CNT. Figure 10c shows the TEM and EDS scan images of the CNTs-diamond interface. The elemental analysis at the CNTs-diamond interface shows that both C from CNTs and C from diamond are tightly combined to form a blended carbon layer.



Figure 9. Structural characteristics of the carbon nanotube/silicon interface: (**a**) SEM image of the CNT-Si interface; (**b**) TEM image of the CNT-Si cross-section; (**c**) TEM image of Ni particles and surrounding carbon nanotubes; and (**d**) TEM image of the CNT-Si interface.



Figure 10. Structure of the diamond-carbon nanotube interface. (**a**,**b**): HRTEM image at the CNTdiamond interface and EDS elemental spectrum along the direction of a single CNT (green line); (**c**) The HRTEM image of the interface between CNT and diamond, and the EDS image of this interface.

We summarize the entire reaction process of growing CNTs on diamond substrates in the schematic diagram provided in Figure 11. Stage I is the thermal annealing (550 °C) that occurs under an H₂ atmosphere in the MPCVD system. Driven by the high temperature, the Ni layer undergoes Oswald ripening, and Ni nanoparticles are formed on the surface of

the substrate. At the same time, Ni and diamond are prone to react to form nickel-carbon compounds such as NiC and Ni₃C under certain temperature conditions [44–47]. Because diamond is pure carbon, it is believed that during the annealing stage, a portion of the Ni reacts with the diamond substrate to form a Ni-C phase, preventing the nickel particles from diffusing. In the growth process of the CNTs (stage II), the external carbon source is introduced and continuously dissolves into the Ni particles, and the CNTs are precipitated after reaching saturation. Since the Ni particles are bound by the C transition layer in the annealing stage (I), most of the Ni particles stay on the surface of the diamond substrate during CNT growth. Furthermore, the Ni particles are always intimately connected to the surface of the diamond surface have the same elemental composition, so there is also a good chemical bonding between the two carbon materials, resulting in a good adhesion force between the later-grown CNT and the diamond.



Figure 11. Reaction process model diagram of the annealing stage (**I**) and carbon nanotube growth stage (**II**) on a diamond substrate.

Through comparison of Figures 8b and 9b, it is seen that the distribution of the Ni particles is quite different in the CNT layers prepared on diamond compared to the Si substrate. In the CNT layer prepared on the diamond substrate, the positions of the Ni particles are almost all located at the junction of the CNT-diamond interface, and it is posited that the growth mode of the CNTs on diamond is primarily the base-growth mechanism [48]. The Ni particles are randomly scattered throughout the CNT layer prepared on the Si substrate, indicating that a significant amount of Ni particles have been separated from the substrate and that the growth mechanism of CNTs is primarily the tip-growth mechanism [49]. Moreover, when CNTs are grown on a diamond substrate, there is a strong interaction between the Ni and the diamond, and most of the Ni particles are "pinned" to the diamond surface for the duration of the growth process, which may also be the reason for the stronger adhesion force between CNTs and diamond substrates.

4. Conclusions

In this work, we fabricated CNTs on diamond and Si substrates via microwave plasma chemical vapor deposition using a Ni catalyst and CH_4 as a carbon source. By studying the growth mode of CNTs and examining their interface bonding properties with diamond and Si substrates, we proposed a model to explain the mechanisms involving both the

catalyst layer's etching and the CNT's growth process on diamond. The basic process for the preparation of nanoscale catalytic particles involves the formation of a catalytic Ni layer with a 10 nm thickness, annealing at 550 °C for 5 min, CNT growth at 600 °C for 30 min, and finally, multi-walled CNTs with a high degree of graphitization are obtained on the diamond substrate. The produced CNTs have a diameter of approximately 15 nm, approximately 10 tube walls, and a strong bonding force between the CNTs and the diamond substrate. The OES analysis results obtained during the MPCVD method of growing CNTs show that the carbon-containing radicals detected in the environment are primarily C2 and CH. The carbon-containing radicals are dissolved upon contact with the Ni catalytic particles, and after reaching saturation, the CNT structure is precipitated and grows at the Ni surface. Analysis of the CNT-diamond bonding interface reveals that the growth mode of the CNTs on the diamond substrate is primarily a base growth mechanism. Additionally, a carbon transition layer with a thickness of approximately 6 nm between the diamond and the CNTs was observed, which may result from the reaction between the Ni and the diamond during the annealing process. Furthermore, this may also be the reason for the strong binding between the CNTs and the diamond substrate.

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References

- 1. Iijima, S. Helical microtubules of graphitic carbon. Nature 1991, 354, 56–58. [CrossRef]
- De Volder, M.F.; Tawfick, S.H.; Baughman, R.H.; Hart, A.J. Carbon nanotubes: Present and future commercial applications. *Science* 2013, 339, 535–539. [CrossRef] [PubMed]
- 3. Lehman, J.; Yung, C.; Tomlin, N.; Conklin, D.; Stephens, M. Carbon nanotube-based black coatings. *Appl. Phys. Rev.* 2018, *5*, 011103. [CrossRef]
- Li, S.; Ma, L.; Long, H.; Yu, X.; Luo, H.; Wang, Y.; Zhu, H.; Yu, Z.; Ma, M.; Wei, Q. Enhanced electron field emission properties of diamond/microcrystalline graphite composite films synthesized by thermal catalytic etching. *Appl. Surf. Sci.* 2016, 367, 473–479. [CrossRef]
- Yang, Z.-P.; Ci, L.; Bur, J.A.; Lin, S.-Y.; Ajayan, P.M. Experimental observation of an extremely dark material made by a low-density nanotube array. *Nano Lett.* 2008, 8, 446–451. [CrossRef]
- 6. Mizuno, K.; Ishii, J.; Kishida, H.; Hayamizu, Y.; Yasuda, S.; Futaba, D.N.; Yumura, M.; Hata, K. A black body absorber from vertically aligned single-walled carbon nanotubes. *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 6044–6047. [CrossRef]
- Holz, T.; Mata, D.; Santos, N.; Bdikin, I.; Fernandes, A.; Costa, F. Stiff diamond/buckypaper carbon hybrids. ACS Appl. Mater. Interfaces 2014, 6, 22649–22654. [CrossRef]
- 8. Ebbesen, T.W.; Ajayan, P.M. Large-scale synthesis of carbon nanotubes. *Nature* 1992, 358, 220–222. [CrossRef]
- Prasek, J.; Drbohlavova, J.; Chomoucka, J.; Hubalek, J.; Jasek, O.; Adam, V.; Kizek, R. Methods for carbon nanotubes synthesis. J. Mater. Chem. 2011, 21, 15872–15884. [CrossRef]
- 10. Koziol, K.; Boskovic, B.O.; Yahya, N. Synthesis of carbon nanostructures by CVD method. In *Carbon and Oxide Nanostructures*; Springer: Berlin, Germany, 2010; pp. 23–49.
- 11. Shah, K.A.; Tali, B.A. Synthesis of carbon nanotubes by catalytic chemical vapour deposition: A review on carbon sources, catalysts and substrates. *Mater. Sci. Semicond. Process.* **2016**, *41*, 67–82. [CrossRef]

- 12. Joselevich, E.; Lieber, C.M. Vectorial growth of metallic and semiconducting single-wall carbon nanotubes. *Nano Lett.* **2002**, *2*, 1137–1141. [CrossRef]
- 13. Uh, H.S.; Lee, S.M.; Choi, S.R.; Park, S.S.; Cho, E.S.; Lee, J.D.; Kwon, S.J. Effect of plasma pretreatment on the structure and emission characteristics of carbon nanotubes. *J. Korean Phys. Soc.* **2003**, *43*, 924–929. [CrossRef]
- Kobashi, K.; Inoue, T.; Tachibana, H.; Kumagai, K.; Miyata, K.; Nishimura, K.; Nakaue, A. Selected-area deposition of diamond films. In *The Physics and Chemistry of Carbides, Nitrides and Borides*; Springer: Berlin, Germany, 1990; pp. 159–167.
- 15. Talapatra, S.; Kar, S.; Pal, S.; Vajtai, R.; Ci, L.; Victor, P.; Shaijumon, M.; Kaur, S.; Nalamasu, O.; Ajayan, P. Direct growth of aligned carbon nanotubes on bulk metals. *Nat. Nanotechnol.* **2006**, *1*, 112–116. [CrossRef] [PubMed]
- 16. Hata, K.; Futaba, D.N.; Mizuno, K.; Namai, T.; Yumura, M.; Iijima, S. Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes. *Science* 2004, *306*, 1362–1364. [CrossRef]
- 17. Cheung, C.L.; Kurtz, A.; Park, H.; Lieber, C.M. Diameter-controlled synthesis of carbon nanotubes. J. Phys. Chem. B 2002, 106, 2429–2433. [CrossRef]
- Murakami, T.; Sako, T.; Harima, H.; Kisoda, K.; Mitikami, K.; Isshiki, T. Raman study of SWNTs grown by CCVD method on SiC. *Thin Solid Film.* 2004, 464, 319–322. [CrossRef]
- 19. Kumar, M.; Ando, Y. A simple method of producing aligned carbon nanotubes from an unconventional precursor–Camphor. *Chem. Phys. Lett.* **2003**, *374*, 521–526. [CrossRef]
- Colomer, J.-F.; Stephan, C.; Lefrant, S.; Van Tendeloo, G.; Willems, I.; Konya, Z.; Fonseca, A.; Laurent, C.; Nagy, J.B. Large-scale synthesis of single-wall carbon nanotubes by catalytic chemical vapor deposition (CCVD) method. *Chem. Phys. Lett.* 2000, 317, 83–89. [CrossRef]
- 21. Willems, I.; Kónya, Z.; Colomer, J.-F.; Van Tendeloo, G.; Nagaraju, N.; Fonseca, A.; Nagy, J.B. Control of the outer diameter of thin carbon nanotubes synthesized by catalytic decomposition of hydrocarbons. *Chem. Phys. Lett.* **2000**, *317*, 71–76. [CrossRef]
- 22. Ward, J.; Wei, B.; Ajayan, P. Substrate effects on the growth of carbon nanotubes by thermal decomposition of methane. *Chem. Phys. Lett.* **2003**, *376*, 717–725. [CrossRef]
- 23. Ago, H.; Nakamura, K.; Imamura, S.; Tsuji, M. Growth of double-wall carbon nanotubes with diameter-controlled iron oxide nanoparticles supported on MgO. *Chem. Phys. Lett.* **2004**, *391*, 308–313. [CrossRef]
- 24. Szabó, A.; Méhn, D.; Kónya, Z.; Fonseca, A.; Nagy, J.B. "Wash and go": Sodium chloride as an easily removable catalyst support for the synthesis of carbon nanotubes. *PhysChemComm* **2003**, *6*, 40–41. [CrossRef]
- Bonard, J.-M.; Klinke, C.; Dean, K.A.; Coll, B.F. Degradation and failure of carbon nanotube field emitters. *Phys. Rev. B* 2003, 67, 115406. [CrossRef]
- 26. Neves, A.; Nazaré, M.H. Properties, Growth and Applications of Diamond; IET: London, UK, 2001.
- 27. Tong, T.; Zhao, Y.; Delzeit, L.; Kashani, A.; Meyyappan, M.; Majumdar, A. Dense vertically aligned multiwalled carbon nanotube arrays as thermal interface materials. *IEEE Trans. Compon. Packag. Technol.* **2007**, *30*, 92–100. [CrossRef]
- 28. Takagi, D.; Kobayashi, Y.; Homma, Y. Carbon nanotube growth from diamond. J. Am. Chem. Soc. 2009, 131, 6922–6923. [CrossRef]
- 29. Varanasi, C.; Petry, J.; Brunke, L.; Yang, B.; Lanter, W.; Burke, J.; Wang, H.; Bulmer, J.; Scofield, J.; Barnes, P. Growth of high-quality carbon nanotubes on free-standing diamond substrates. *Carbon* **2010**, *48*, 2442–2446. [CrossRef]
- Varshney, D.; Ahmadi, M.; Guinel, M.J.; Weiner, B.R.; Morell, G. Single-step route to diamond-nanotube composite. *Nanoscale Res.* Lett. 2012, 7, 1–6. [CrossRef]
- 31. Wang, X.; Li, Q.; Xie, J.; Jin, Z.; Wang, J.; Li, Y.; Jiang, K.; Fan, S. Fabrication of ultralong and electrically uniform single-walled carbon nanotubes on clean substrates. *Nano Lett.* **2009**, *9*, 3137–3141. [CrossRef]
- Ding, F.; Rosén, A.; Bolton, K. Molecular dynamics study of the catalyst particle size dependence on carbon nanotube growth. J. Chem. Phys. 2004, 121, 2775–2779. [CrossRef]
- 33. Guéret, C.; Daroux, M.; Billaud, F. Methane pyrolysis: Thermodynamics. Chem. Eng. Sci. 1997, 52, 815–827. [CrossRef]
- Mubarak, N.; Yusof, F.; Alkhatib, M. The production of carbon nanotubes using two-stage chemical vapor deposition and their potential use in protein purification. *Chem. Eng. J.* 2011, 168, 461–469. [CrossRef]
- 35. Taft, E.; Philipp, H. Optical properties of graphite. Phys. Rev. 1965, 138, A197. [CrossRef]
- Tang, T.; Chen, X.; Meng, X.; Chen, H.; Ding, Y. Synthesis of multiwalled carbon nanotubes by catalytic combustion of polypropylene. *Angew. Chem. Int. Ed.* 2005, 44, 1517–1520. [CrossRef]
- 37. Noda, S.; Hasegawa, K.; Sugime, H.; Kakehi, K.; Zhang, Z.; Maruyama, S.; Yamaguchi, Y. Millimeter-thick single-walled carbon nanotube forests: Hidden role of catalyst support. *Jpn. J. Appl. Phys.* **2007**, *46*, L399. [CrossRef]
- Göldel, A.; Kasaliwal, G.R.; Pötschke, P.; Heinrich, G. The kinetics of CNT transfer between immiscible blend phases during melt mixing. *Polymer* 2012, 53, 411–421. [CrossRef]
- Qin, Y.; Hu, M. Field emission properties of electrophoretic deposition carbon nanotubes film. *Appl. Surf. Sci.* 2009, 255, 7618–7622.
 [CrossRef]
- Su, H.-C.; Chen, C.-H.; Chen, Y.-C.; Yao, D.-J.; Chen, H.; Chang, Y.-C.; Yew, T.-R. Improving the adhesion of carbon nanotubes to a substrate using microwave treatment. *Carbon* 2010, *48*, 805–812. [CrossRef]
- Chen, Z.; Zhang, Q.; Lan, P.; Zhu, B.; Yu, T.; Cao, G.; den Engelsen, D. Ultrahigh-current field emission from sandwich-grown well-aligned uniform multi-walled carbon nanotube arrays with high adherence strength. *Nanotechnology* 2007, 18, 265702. [CrossRef] [PubMed]

- 42. Lahiri, I.; Lahiri, D.; Jin, S.; Agarwal, A.; Choi, W. Carbon nanotubes: How strong is their bond with the substrate? *ACS Nano* **2011**, *5*, 780–787. [CrossRef]
- Jiang, Y.; Deng, Z.; Zhou, B.; Wei, Q.; Long, H.; Wang, Y.; Li, J.; Hu, N.; Ma, L.; Lin, C.-T. Nickel-induced transformation of diamond into graphite and carbon nanotubes and the electron field emission properties of resulting composite films. *Appl. Surf. Sci.* 2018, 428, 264–271. [CrossRef]
- Ostapenko, R.; Ivanenko, K.; Kuryliuk, A.; Nakonechna, O.; Belyavina, N. Synthesis and characterization of the novel nanostructured NiC carbide obtained by mechanical alloying. *Adv. Powder Technol.* 2022, 33, 103390. [CrossRef]
- 45. Kovács, G.J.; Koós, A.; Bertoni, G.; Sáfrán, G.; Geszti, O.; Serin, V.; Colliex, C.; Radnóczi, G. Structure and spectroscopic properties of C–Ni and CN x–Ni nanocomposite films. *J. Appl. Phys.* **2005**, *98*, 034313. [CrossRef]
- 46. Seah, C.-M.; Vigolo, B.; Chai, S.-P.; Ichikawa, S.; Gleize, J.; Le Normand, F.; Aweke, F.; Mohamed, A.R. Sequential synthesis of free-standing high quality bilayer graphene from recycled nickel foil. *Carbon* **2016**, *96*, 268–275. [CrossRef]
- 47. Fang, C.; Sluiter, M.; Van Huis, M.; Zandbergen, H. Structural and magnetic properties of NiC x and NiN x (x= 0 to 1 3) solid solutions from first-principles calculations. *Phys. Rev. B* 2012, *86*, 134114. [CrossRef]
- Gavillet, J.; Loiseau, A.; Journet, C.; Willaime, F.; Ducastelle, F.; Charlier, J.-C. Root-growth mechanism for single-wall carbon nanotubes. *Phys. Rev. Lett.* 2001, 87, 275504. [CrossRef] [PubMed]
- Kong, J.; Soh, H.T.; Cassell, A.M.; Quate, C.F.; Dai, H. Synthesis of individual single-walled carbon nanotubes on patterned silicon wafers. *Nature* 1998, 395, 878–881. [CrossRef]