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Research Article

Controlled Geometry Formation of the Carbon Coils by the Substrate Pretreatment

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Carbon coils could be synthesized using C_2H_2/H_2 as source gases and SF_6 as an incorporated additive gas under thermal chemical vapor deposition system. Prior to the carbon coils deposition reaction, the supporting substrates were pretreated using various methods. Among the methods, the thermal etching pretreatment of Ni-SiO_2 substrate with SF_6 leads to the exclusive formation of the nanosized carbon coils. The diamond powders pretreatment of Si substrate gives rise to the dominant formation of the microsized carbon coils after 10 minutes reaction time. The geometry selectivity for the carbon coils in a specific pretreatment method was discussed in association with the peeled-off Ni layers by the thermal etching pretreatment with SF_6 and the remained carbon particles on Si substrate by the diamond powders pretreatment.

1. Introduction

Although the unique geometries of the carbon coils have been attracted as the promising potential materials in nano-/microelectronics or mechanics [1–4], the controlled geometry for as-grown carbon coils should be preferentially solved to practically apply them in diverse application fields [5, 6].

The metal catalyst was regarded as one of the indispensable factors for the formation of the carbon coils [7–11]. In addition, the characteristics of the used metal catalyst seem to affect the formation density and the geometry of the carbon coils via the vapor-liquid-solid growth mechanism of the carbon nanomaterials [9–13]. Meanwhile, the property of the supporting substrate may alternate the characteristics of the used metal catalyst, consequently affecting the formation density and the geometries of the as-grown carbon coils [13, 14]. Until now, Huang et al. reported that the formation of the carbon nanocoils would be critically affected by the morphology change of Si substrate which was induced by the HF solution corrosion [15]. They found the coils formation exclusively on the concavo-convex surface morphology of Si substrate with the straight carbon nanotubes on the flat Si surface, namely, on noncorroded Si surface. Veziri et al. demonstrated that the morphology of the carbon nanostructures grown by chemical vapor deposition (CVD) on the porous supports is strongly affected by the porosity of the supporting substrate [16]. Bai obtained a more or less controlled morphology of the carbon coils through the careful choice of alumina substrate pore size [17]. Despite many efforts to enhance the controlled geometry for the carbon coils, detailed reports regarding the effect of the substrate pretreatment on the formation of the carbon coils are still required.

This work introduces the geometry selectivity for the as-grown carbon coils by the pretreatment of the substrate surface. Prior to the carbon coils deposition reaction, the pretreatment of the supporting substrates (Si and SiO_2 substrates) was carried out using diamond powders, SiC sandpaper, and thermal etching with SF_6. To elucidate the exact cause for the exclusive growth of the carbon coils having the controlled geometry, systematic investigations for the substrate pretreatment effect were carried out and discussed.

2. Experimental Details

For silicon substrate, p-type Si (100) substrates were used. For its oxide substrate, SiO_2 layered Si substrates were employed. SiO_2 layered Si substrates in this work were prepared by the

thermal oxidation of $2.0 \times 2.0\ cm^2$ p-type Si (100) substrates. The thickness of silicon oxide (SiO_2) layer on Si substrate was estimated to be about 300 nm.

Four kinds of the pretreatment methods were performed as follows.

(a) Method-A, the substrates were pretreated by the diamond powders: the diamond powders pretreatment was carried out by an ultrasonic treatment for 60 minutes using about 0.5 g diamond powders in an acetone solution. Various micrometer sizes of synthetic diamond particles were used as diamond powders.

(b) Method-B, the substrates were pretreated by SiC sand paper: unidirectional scratching using SiC sand paper was carried out for several times. The grain size of SiC was around 70 μm in diameter.

(c) Method-C, the substrates were pretreated by thermal etching with SF_6: in this case, the substrates were heated up to 750°C in the thermal CVD reactor. And then, pure H_2 flow (35 sccm) + SF_6 flow (35 sccm) were injected into the reactor up to 100 torr total pressure. After 5 minutes, the heater and H_2 + SF_6 flow injection were turned off, and then the reactor cooled down in a vacuum state (10^{-2} torr).

(d) Method-D, the substrates were first deposited by Ni thin catalyst layer (about 200 nm thickness), and then they were pretreated by Method-C.

After the pretreatment of the substrate, Ni catalyst layer deposition on the substrates was carried out. For Ni catalyst layer deposition on the substrates, a 0.1 g Ni powder (99.7%) was evaporated for 1 minute to form the Ni catalyst layer on the substrate using thermal evaporator. The estimated Ni catalyst layer on the substrate was about 200 nm.

The carbon coils deposition was performed on the Ni catalyst layer deposited substrates using thermal CVD system. C_2H_2 and H_2 were used as source gases. SF_6, as an incorporated additive gas, was injected into the reactor for 5 minutes during the initial deposition time. The flow rate for C_2H_2, H_2, and SF_6 was fixed at 15, 35, and 35 sccm, respectively. Two kinds of the overall deposition time for as-grown carbon coils were applied in this work. Namely, one is H_2 + C_2H_2 + SF_6 flow for 5 minutes during the initial deposition time and the consecutive H_2 + C_2H_2 flow for 5 minutes, and another is H_2 + C_2H_2 + SF_6 flow for 5 min during the initial deposition time and the consecutive H_2 + C_2H_2 flow for 55 minutes. The reaction conditions with the various substrates and the pretreatment methods were shown in Table 1.

The morphologies of the carbon coils-deposited substrates were investigated using field emission scanning electron microscopy (FESEM). Compositional analysis was performed by X-ray photoelectron spectroscopy (XPS).

3. Results and Discussion

Ten samples (samples A~J) having the different substrates and the pretreatment methods were prepared as shown in Table 1. Substrates A~J were placed in the substrate holder (Al_2O_3 boat), and the syntheses of the carbon coils were simultaneously carried out on substrates A~J. Indeed, the different supporting substrates (Si and SiO_2 substrates) having the different pretreatment methods were simultaneously mounted on the substrate holder in the reaction chamber. So, the carbon coils formation reaction on the different supporting substrates with the different pretreatment methods would have an identical experimental condition.

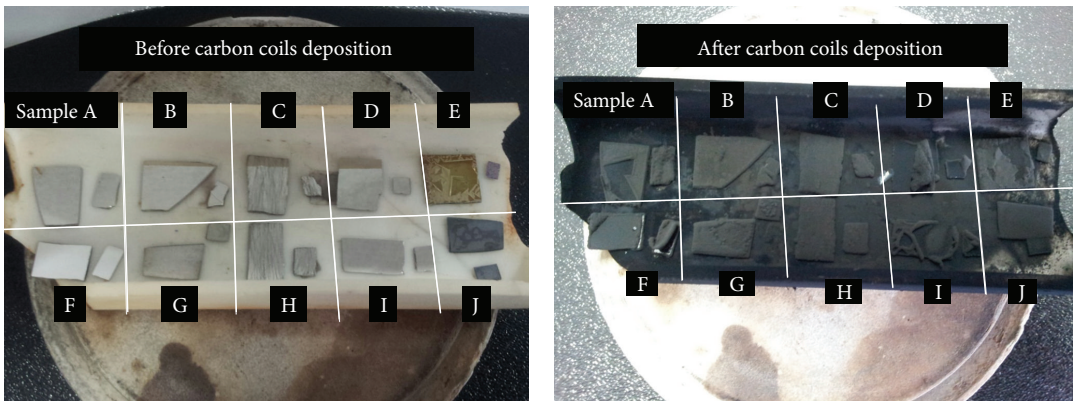
Figures 1(a) and 2(a) show the prepared substrates by the various pretreatment methods. Figures 1(b) and 2(b) show the as-grown carbon coils on these substrates after 10 minutes (Figure 1(b)) and 60 minutes (Figure 2(b)) deposition reactions. As a naked eye, a lot of carbon materials seemed to be formed on the samples. For the nontreated substrate case, we could observe the formation of a lot of delaminated carbon-related materials on the samples surfaces, irrespective of the deposition times (see samples D and I in Figures 1(b) and 2(b)). On the other hand, the pretreatment of the substrate seems to reduce the delaminated phenomena (compare samples D and I with the others in Figures 1(b) and 2(b)).

Microscopic images for the as-grown carbon materials were also investigated using FESEM. Figure 3 shows FESEM images revealing the formation of the as-grown carbon coils on the various substrates after 10 minutes deposition time. Figure 4 shows the magnified FESEM images for Figure 3. For the thermal etching with SF_6 on Ni-SiO_2 substrate, noticeably, the nanosized carbon coils were exclusively formed on SiO_2 substrate as shown in Figures 3(e) and 4(e). For the diamond powders-pretreated substrate, meanwhile, the microsized carbon coils having a few micrometer-sized coil diameters were mostly observed on Si substrate as shown in Figures 3(f) and 4(f). Except samples E and F, both the nanosized carbon coils and the microsized ones were simultaneously observed on the samples. This result reveals that the selective formation of the carbon coils having specific geometry could be possible merely by the pretreatment of the different substrates, namely, the diamond powders pretreatment of Si substrate (Method-A) for the microsized carbon coils and the thermal etching pretreatment of Ni-SiO_2 substrate with SF_6 (Method-C) for the nanosized carbon coils.

To investigate the detailed geometry for the as-grown carbon coils, the high-magnified FESEM image for samples E and F was also carried out. For sample E, the occurrence of the square-type shapes on the substrate in Figure 5(a) seems to be due to the thermal etching with SF_6 during the reaction. Most of the nanosized carbon coils in sample E have wave-like nanosized coil type geometry [18] with a diameter of less than 0.3 μm. They seem to form a matrix of the wave-like nanosized coils (see Figures 5(b) and 5(c)). For sample F, the formation of the microsized carbon coils having almost the constant coil pitch of ~0.2 μm without any coil gap could be observed as shown in Figures 5(d)~5(f). The diameters of these coils are around 2.0 μm, and the lengths of these coils were estimated to be several tens of micrometers. The carbon nanofilaments that built up the microsized carbon coil have a circular type shape with a diameter of ~0.5 μm. These carbon nanofilaments seem to be composed by two kinds

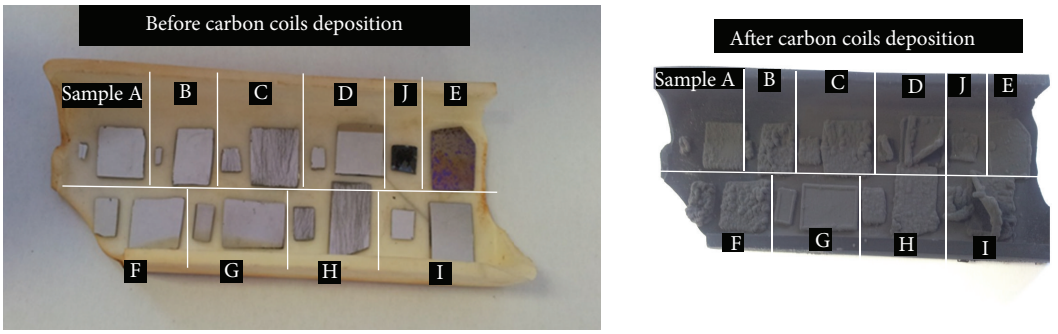
Table 1: Experimental conditions for the deposition of the carbon coils on Si or SiO_2 substrate with the different pretreatment methods.

Sample	Substrate	Pretreatment method	C_2H_2 flow rate (sccm)	H_2 flow rate (sccm)	SF_6 flow rate (sccm)	Total pressure (torr)	Total deposition times (min)	Source gases flow time (min)			Substrate temp. (°C)
								C_2H_2	H_2	SF_6	
A	SiO_2	Method-A	15	35	35	100	10, 60	10, 60	10, 60	5	750
B	SiO_2	Method-B	15	35	35	100	10, 60	10, 60	10, 60	5	750
C	SiO_2	Method-C	15	35	35	100	10, 60	10, 60	10, 60	5	750
D	SiO_2	None	15	35	35	100	10, 60	10, 60	10, 60	5	750
E	Ni-SiO_2	Method-D	15	35	35	100	10, 60	10, 60	10, 60	5	750
F	Si	Method-A	15	35	35	100	10, 60	10, 60	10, 60	5	750
G	Si	Method-B	15	35	35	100	10, 60	10, 60	10, 60	5	750
H	Si	Method-C	15	35	35	100	10, 60	10, 60	10, 60	5	750
I	Si	None	15	35	35	100	10, 60	10, 60	10, 60	5	750
J	Ni-Si	Method-D	15	35	35	100	10, 60	10, 60	10, 60	5	750



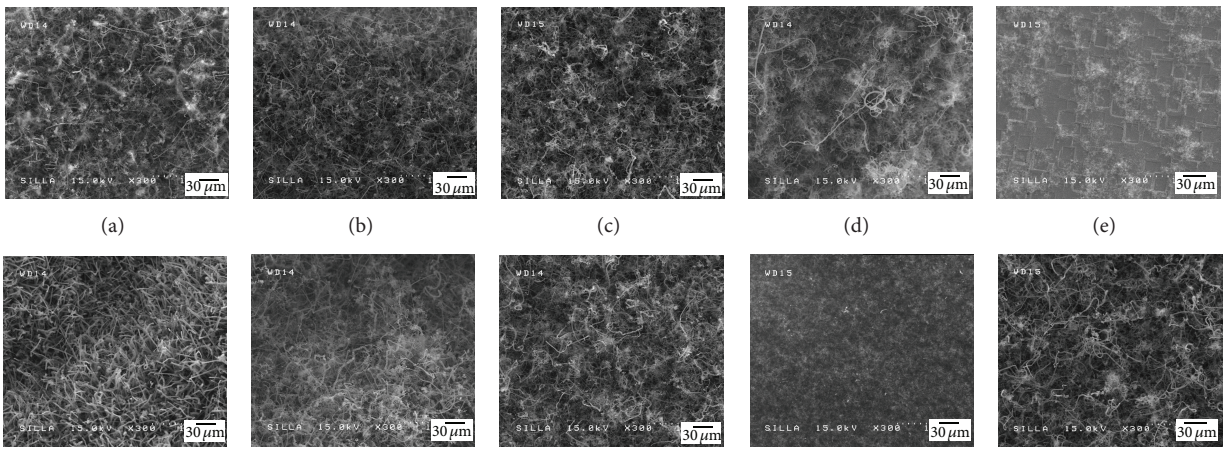
(a) (b)

Figure 1: Photographs of (a) the prepared substrates by the various pretreatment methods and (b) the as-grown carbon coils on these substrates after 10 minutes deposition reaction. Two pieces were shown for each sample. The small piece was used for FESEM investigation.



(a) (b)

Figure 2: Photographs of (a) the prepared substrates by the various pretreatment methods and (b) the as-grown carbon coils on these substrates after 60 minutes deposition reaction. Two pieces were shown for each sample. The small piece was used for FESEM investigation.



(a) (b) (c) (d) (e)

(f) (g) (h) (i) (j)

Figure 3: FESEM images for the surface morphologies of the samples after 10 minutes deposition reaction for (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E, (f) sample F, (g) sample G, (h) sample H, (i) sample I, and (j) sample J.

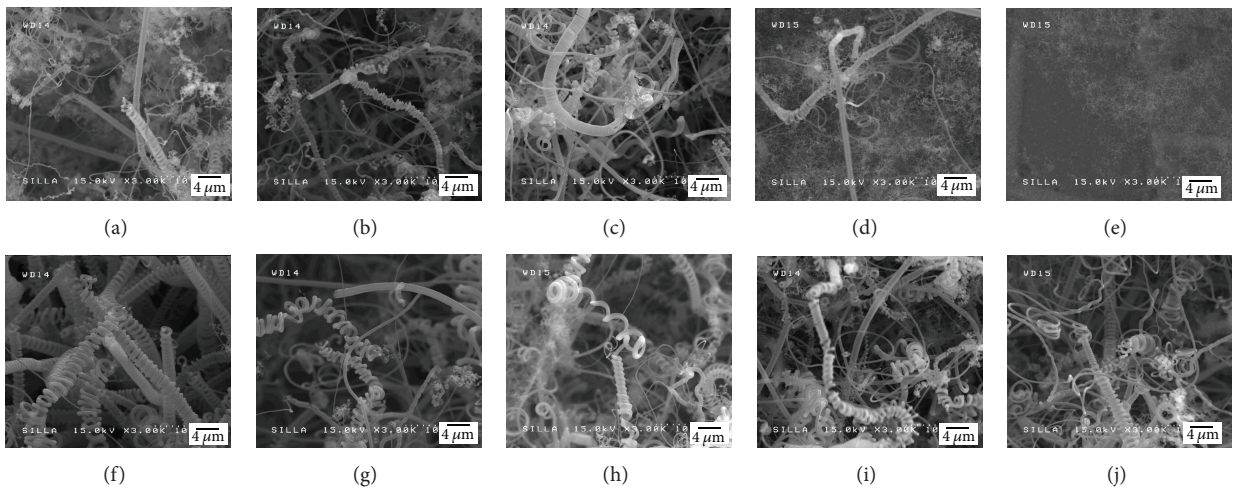


Figure 4: Magnified FESEM images for the surface morphologies of the samples after 10 minutes deposition reaction for (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E, (f) sample F, (g) sample G, (h) sample H, (i) sample I, and (j) sample J.

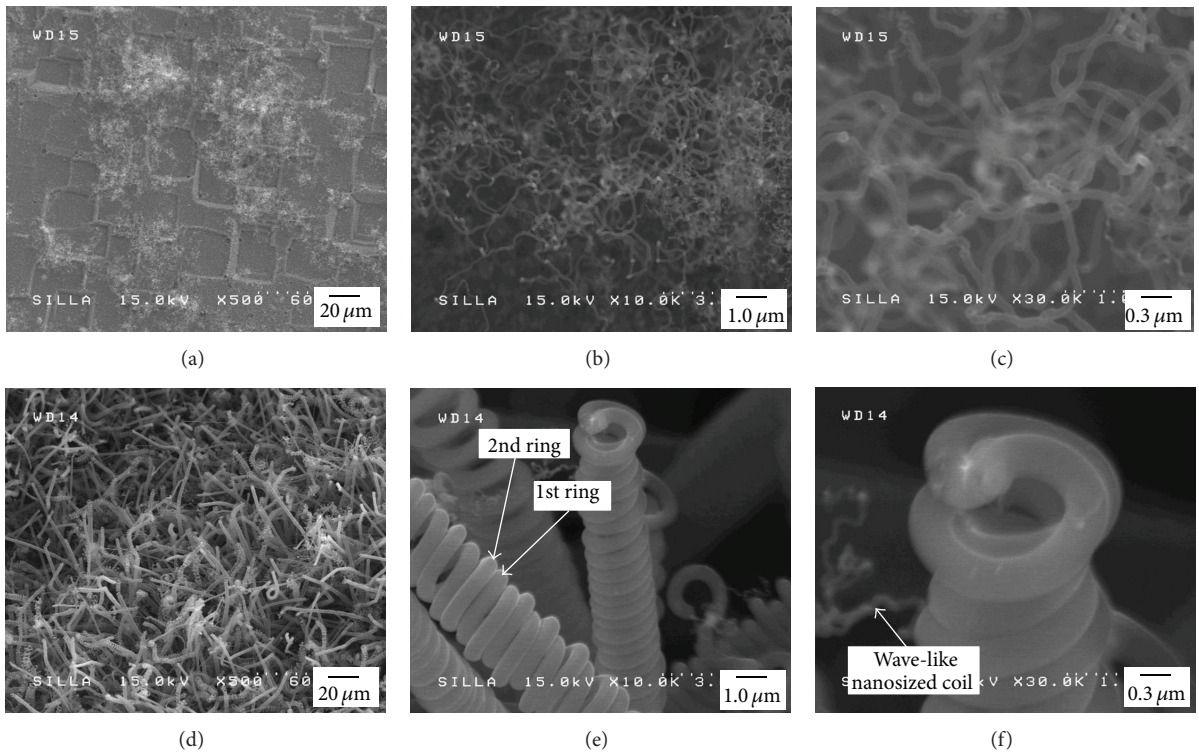


Figure 5: FESEM images for the surface morphologies of the samples after 10 minutes deposition reaction for sample E under the magnification of (a) 500, (b) 10,000, and (c) 30,000 and for sample F under the magnification of (d) 500, (e) 10,000, and (f) 30,000.

of the different ring-type shapes (see the first and second rings in Figure 5(e)). It indicates that the microsized carbon coils formation of this work follows the typical double-helix type geometry. Around the microsized carbon coils, the tiny wave-like nanosized coils were also observed, as shown in Figure 5(f).

After 60 minutes reaction, sample E still reveals the exclusive formation of the nanosized carbon coils, while the other samples show the carbon coils having various geometries (compare Figure 6(e) with the other images in Figure 6). The combined results of Figures 4 and 6 confirm that the exclusive formation of the nanosized carbon coils could be possible by the thermal pretreatment of Ni-SiO_2 substrate with SF_6 regardless of the deposition time. For the diamond powders pretreatments on the substrate, meanwhile, only sample F (Si substrate) at the relatively short reaction time (10 minutes) can give the dominant formation of the microsized carbon coils (compare Figures 4(f) with 6(f)).

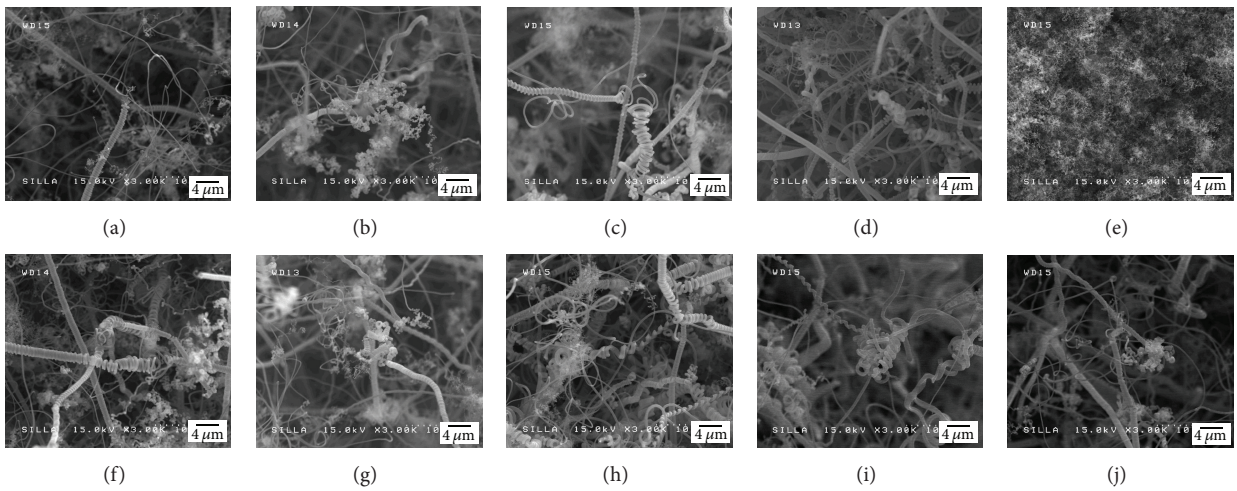


Figure 6: Magnified FESEM images for the surface morphologies of the samples after 60 minutes deposition reaction for (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E, (f) sample F, (g) sample G, (h) sample H, (i) sample I, and (j) sample J.

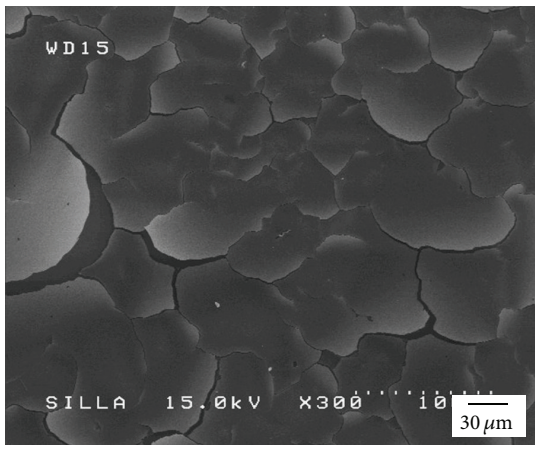


Figure 7: FESEM images indicating the situation of the peeled-off Ni layers from Ni-SiO_2 substrate by the thermal pretreatment with SF_6 after cooling down this substrate from 750°C to 25°C under vacuum condition.

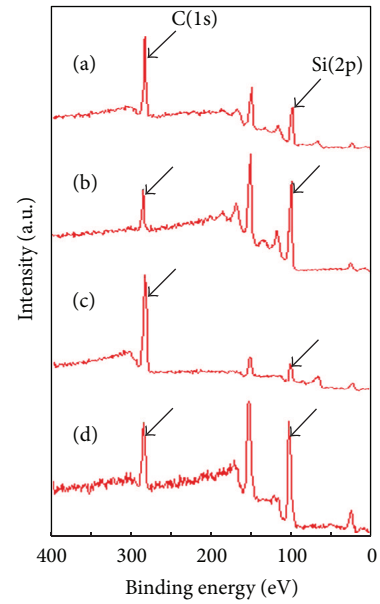


Figure 8: XPS spectra of the substrate surface before the carbon coils deposition reaction for (a) sample A, (b) sample C, (c) sample F, and (d) sample H.

For SiO_2 substrate, the thermal pretreatment with SF_6 seems to increase the stress between the predeposited Ni catalyst layer and SiO_2 substrate. Figure 7 shows FESEM images indicating the situation of the peeled-off Ni layers from the substrate with the thermal pretreatment (sample E) after cooling down the substrate from 750°C to 25°C under vacuum condition. As shown in this image, SiO_2 substrate with the thermal pretreatment gives rise to the flaky state for Ni layer, which may form the nanosized Ni pieces during the reaction. Basically, the mechanism of the carbon coils growth was dependent on the metal size and shape [19]. The nanosized carbon coils were formed from the nanosized Ni pieces, and then they would deposit on the whole surface of the substrate. This seems to be the reason why the thermal pretreatment with SF_6 gives rise to the exclusive formation of the nanosized carbon coils on the entire surface of SiO_2 substrate. For Si substrate, the combined results of samples E and J confirm that the thermal pretreatment with SF_6 on Ni-Si substrate, compared with that on Ni-SiO_2 substrate, shows various geometries for as-grown carbon coils (compare Figures 3(e) with 3(j)). The different thermal expansion coefficient value [20, 21] between the predeposited Ni catalyst layer and the different substrates (SiO_2 or Si substrate) seems to be the main reason for these different results [22].

Figure 8 shows XPS spectra for samples A, C, F, and H, indicating the existence of the carbon component on the surface of the Si or SiO_2 substrate by the pretreatment method-A or -B. $I_{c(1s)}/I_{si(2p)}$ for samples A, C, F, and H were measured to be about 1.49, 0.35, 5.20, and 0.53, respectively. These

results show that the amount of the remained carbon species is largest in the case of Si substrate and the pretreatment method-A combination (sample F) than any other case. It clearly confirms that the diamond powder pretreatment on Si substrate would leave the carbon particles on the surface of the substrate [23]. Therefore, these remained carbon particles seem to effectively motivate the formation of the microsized carbon coils during the relatively short reaction time (10 minutes). At the relatively longer reaction time (90 minutes in this work), on the other hand, the influence of the substrate-remained carbon particles on the geometry formation for as-grown carbon coils seems to be diminished. At this point, therefore, the existence of the remained carbon particles by the diamond powders pretreatment is considered to be the main cause for the dominant formation of the microsized carbon coils on Si substrate during the relatively short reaction time (10 minutes).

4. Conclusion

Diamond powders pretreatment of Si substrate left the carbon particles on the substrate surface. The remained carbon particles are considered to be the main cause for the formation of the dominant formation of the microsized carbon coils after the relatively short reaction time (10 minutes). Thermal etching pretreatment of Ni-SiO_2 substrate with SF_6 exclusively produces the nanosized carbon coils. The great difference of the thermal expansion coefficient value between the predeposited Ni catalyst layer and SiO_2 substrate seems to develop the nanosized Ni pieces during the carbon coils deposition reaction. Eventually, it produces the exclusive formation of the nanosized carbon coils on the entire surface of SiO_2 substrate.

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