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# Growth of carbon with vertically aligned nanoscale flake structure in capacitively coupled rf glow discharge

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**Abstract**

Carbon nanoflakes (CNFs) have been deposited on Si (1 0 0) wafer substrates at a substrate temperature of 670 °C from a glassy carbon target by capacitively coupled rf (13.56 MHz) glow discharge using a mixture discharge gas of Ar and $CH_4$ with a total pressure of 14.5 Pa. Microstructures of deposited carbon were investigated by a field emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM). Under the given conditions, vertically aligned CNFs with a flake length of about 1 μm and thickness of about 20 nm were grown. High intensity and symmetry of electron diffraction pattern indicate that the CNFs deposited by capacitively coupled rf glow discharge have three-dimensionally perfect crystallinity with a graphene interlayer spacing of 335 pm. In particular, there is little disorder in stacking of the layer structure. It was further found that the thickness of the flakes was less dependent of deposition time while the length of the flakes increases to about 1 μm with increasing deposition time to 3 h. The growth rate of a graphite sheet parallel to (0 0 1) stacking layers was much higher than that perpendicular to (0 0 1) stacking layer, resulting in anisotropic growth of a flake-like structure. The formation mechanisms of CNFs are discussed from the viewpoint of the difference in residence time of carbon atoms on CNF surfaces parallel to and perpendicular to (0 0 1) direction and anisotropic heat conductivity of graphite.


*Keywords:* Carbon; Nanostructure; Nanoflake; rf Glow discharge

## 1. Introduction

Nanostructure materials are known to exhibit novel and technologically attractive properties due to quantum size effects, surface effects, small grain size effects, etc. [1]. Among nanomaterials, as a versatile element constructing the various allotropes such as diamond, graphite, fullerenes and nanotubes, carbon nanoscaled materials have been paid much more attention recently. The high Young's modulus of about 1.8 MPa, diameter-dependent electric conductivity, and a very low onset of electric field for electron emission have made the carbon nanotubes (CNTs) to be one of the most studied nanomaterials in the past decade [2]. Carbon can also constitute other interesting types of the nanoscale allotrope: fullerene and carbon nanoflakes (CNFs). Between these two nanoscale allotropes, CNF has captured more attention because of its interesting chemical, electrical, and mechanical properties. One of the interesting chemical properties is a high ability as catalysis matrix. In graphite, the weak van-der-Waals bonding between two graphene layers allows atoms or molecules to be intercalated into them. In CNFs, a high density of open edges of (1 0 1) and (1 1 2) surfaces and a high specific surface area further increase chemical reactivity [3]. Another interesting application of CNF is for field emission devices. Shang et al. [4] reported that aligned nanoflake films showed an electron emission turn-on field of about 17 MV/m and might have a potential application in vacuum electronic devices. CNFs can be introduced into other application fields such as electrode [5,6], hydrogen

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storage materials [7], lubricant [8]. In addition, CNFs have the remarkable advantage over CNTs in fabrication because in the growth of CNFs metal catalysts, high substrate temperature and catalyst passivation needed for CNTs growth [9] are not required. Practical applications can be more expected on the CNFs in the field of nanostructured materials.

To date, several methods have been proposed to synthesize the CNFs or nanowalls: arc discharge evaporation [10], laser ablation [11], microwave plasma enhanced chemical vapor deposition [12], and the hot-filament chemical vapor deposition (HFCVD) [4,13]. Regarding the carbon electrode arc-discharging and laser ablation, CNFs usually coexist with nanotubes and other soot, in addition to metal catalyst dopants. The yield CNFs was low when the above methods were applied. Tungsten filaments have to be heated to 2100 °C in HFCVD, resulting in around 3% tungsten contamination from filaments contained in the CNF films [4].

In the present paper, we have deposited CNFs by capacitively coupled rf magnetron discharge using a glassy carbon target as an electrode. By this method, a large area growth of aligned and relatively pure CNFs grown perpendicular to the substrate could be achieved, meanwhile, the deposition method using capacitively coupled rf magnetron glow discharge can overcome the shortcoming of the previously referred methods. Microstructures of the CNFs will be investigated by field emission scanning electron microscope (FESEM) and high-resolution transmission electron microscope (HRTEM). Growth mechanisms of the nanoflakes will be also discussed.

## 2. Experimental procedure

### 2.1. Deposition process

The apparatus used in this study was a load lock-type sputtering machine (SPC-350UHV: ANELVA corporation), schematically shown in Fig. 1. A glassy carbon disk with 75 mm diameter was set to one of the five cathodes equipped in the high vacuum deposition chamber. The distance between the target surface and the substrate is about 60 mm. The deposition chamber was evacuated to a base pressure lower than $1.0 \times 10^{-5}$ Pa prior to deposition runs by a turbo molecular pump. As substrates, silicon (1 0 0) wafers ultrasonically cleaned were used. rf power applied to the target was 100 W. The mixture of Ar (99.998% in purity) and $CH_4$ (99.9% in purity) was used as a discharge gas. Their flow rates were controlled to be at 14 and 28 sccm, respectively. The total pressure was controlled to be approximately 14.5 Pa. The substrate was heated to 670 °C by lamp heaters set behind the substrate holder.

### 2.2. Film analysis

A FESEM (S-4500: Hitachi) was used to observe the morphology of deposited films and to measure thickness,

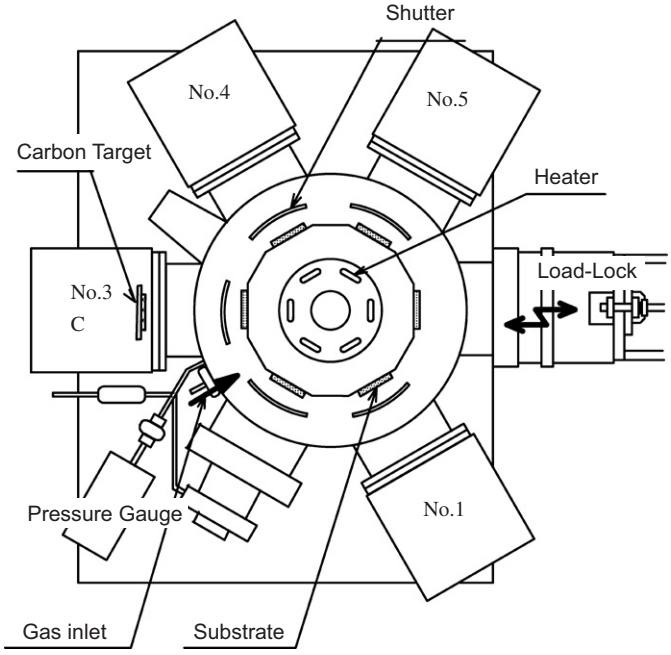


Fig. 1. Schematic of the sputtering apparatus used in the experiment.

length, and width of grown nanoflakes. A transmission electron microscope (TEM, HF-2000: Hitachi) with a field-emission electron gun operated at 200 kV was used to observe microstructure of nanoflakes. Cross-sectional TEM specimens were prepared with argon ion-thinning.

## 3. Results

Fig. 2 shows FESEM images of CNFs grown on silicon substrates at 670 °C for various discharge durations. Vertically well-aligned CNFs are observed for all the samples. A typical size of the nanoflakes grown for 3 h is a length of 1 μm, a width of 600 nm, and a thickness of 30 nm. In Fig. 3, SEM top view images of nanoflakes are shown. It is clear that the flakes are not flat but in "S" or "C" shapes. It was found by SEM observation that the condition needed to grow the flake-like structure is a substrate temperature of $>600$ °C and a $CH_4$ partial pressure of $>6.8$ Pa.

In Fig. 4(a), an HRTEM image of a sheet of CNFs is shown. A layered structure in a sheet of flakes is clear. The number of layers in one piece is about 30. In Figs. 4(b) and (c), TEM diffraction patterns are shown for the flake shown in Fig. 4(a), with the electron beam normal to and parallel to the layers. The diffraction pattern shown in Fig. 4(b) is six-fold and of hexagonal closed packed structure (HCP). Two bright spots in Fig. 4(c) assigned to those from (0 0 2) planes and concentric. From these two spots, layer spacing was calculated to be 335 pm, which well agrees to the value obtained for graphite crystal without disorder of stacking [14]. Furthermore, the weak spots of (1 0 1) groups also appear. It is clearly shown from the two diffraction patterns in Figs. 4(b) and (c) that a