SYNTHESIS OF CARBON NANOWALLS (CNWs) ON A SiO₂ SUBSTRATE BY MICROWAVE PLASMA-ENHANCED CHEMICAL VAOOR DEPOSITION (MPECVD) WITHOUT CATALYST

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ABSTRACT

Carbon nanowalls(CNWs) sheets have been synthesized by microwave plasma enhanced chemical vapor deposition(MPECVD) using mixture of C_2H_2 and H_2 gases on SiO_2 substrates. It is revealed that the CNWs are grown at the fine-textured structure on the SiO_2 and the growth process does not require the catalyst. The effect of microwave power on surface morphology has been investigated. Continuous increase in height and decrease in width of carbon walls with increasing reaction time have been observed by scanning electron microscopy (SEM). Raman spectroscopy of these films revealed characteristics of disordered microcrystalline graphite. Possible growth mechanism of carbon nanowalls has been discussed with time evolution of surface microstructure.

Keywords: CNWs, MPECVD, catalyst, growth mechanism

INTRODUCTION

During last decade, much attention has been paid towards synthesis and characterization of the nano-structured carbon materials such as CNTs, carbon nanoparticles (CNPs), carbon nano-sheets, carbon nano-horns, etc [1]. In particular, the CNWs, which are two-dimensional stacked graphene sheets vertically standing on substrates, are promising for applications in various devices, owing to their high aspect ratio, large specific surface area, high carrier mobility, and large current-carrying capability[2-5]. The interfacial layer, which is grown at an initial stage of CNWs growth between the CNWs and substrates, is also essential to the crystalline structures and electrical properties of CNWs [6]. Therefore, it is important to investigate the crystalline structures of CNWs and interfacial layers. However, it is difficult in general to evaluate the crystalline structures of nanomaterials such as CNWs using laboratory equipment, since most of them have quite low coverage and filling fraction on the substrate surfaces [7]. Several methods, including arc discharge [1], laser ablation [9], various types of chemical vapor deposition (CVD) with or without plasma assistance [10-13], have been used for the growth of carbon nanomaterials. The morphologies of CNWs are controllable by varying the gas flow rate ratio, growth temperature and time evolution, MPECVD has been widely used for the growth of different carbon nanostructures such as carbon nanotubes, carbon nano-sheets, and diamond films [14-17]. MPCVD was recently used to grow vertically oriented on a variety of substrates, and graphite flakes have been deposited on the walls of a stainless steel microwave MPCVD chamber [18]. DC arc discharge of graphitic electrodes has also been shown to yield petal-like graphite sheets [19]. Mixtures of H_2 and He suitably proportioned in an arc discharge can also be used to improve graphene growth , with the hypothesis that H_2 serves to terminate the dangling bonds in the evaporated graphite thereby preventing it to form

closed structures such as CNTs. Microwave plasma operating at low pressure is a kind of low temperature plasma which is due to the non-equilibrium state between electrons and other heavy particles in plasma space and is full of active species[20]. Hence MPECVD technique could be effectively used to synthesize carbon nanostructures at low temperatures. In this paper, the growth time dependence of CNWs formed by MPECVD is investigated, and we report for the synthesis of high density and uniformly distributed CNWs on SiO_2 (p-type,100) substrates by MPECVD technique at relatively non - catalytic method using H_2 and C_2H_2 mixture as precursor gases.

EXPERMENTAL AND THEORETICAL METHODS

CNWs were synthesized using tubular MPECVD system, consisting of a quartz tube of inner diameter 250 mm inserted into the waveguide. A 400 W, 2.45GHz power source was used along with the standard isolator, three stub tuner and sliding short circuit. One end of the quartz tube was coupled to a vacuum pumping system. The other end of the tube was fixed to a gas line connected to H_2 and C_2H_2 gases through mass flow controllers (MFC). P-type Si (100) substrates were ultrasonically cleaned in hydrofluoric acid, acetone, trichloroethylene and isopropyl alcohol, respectively. The Si substrate was then loaded in the MPECVD system on a quartz boat positioning the substrate at the intersection of quartz cavity and waveguide.
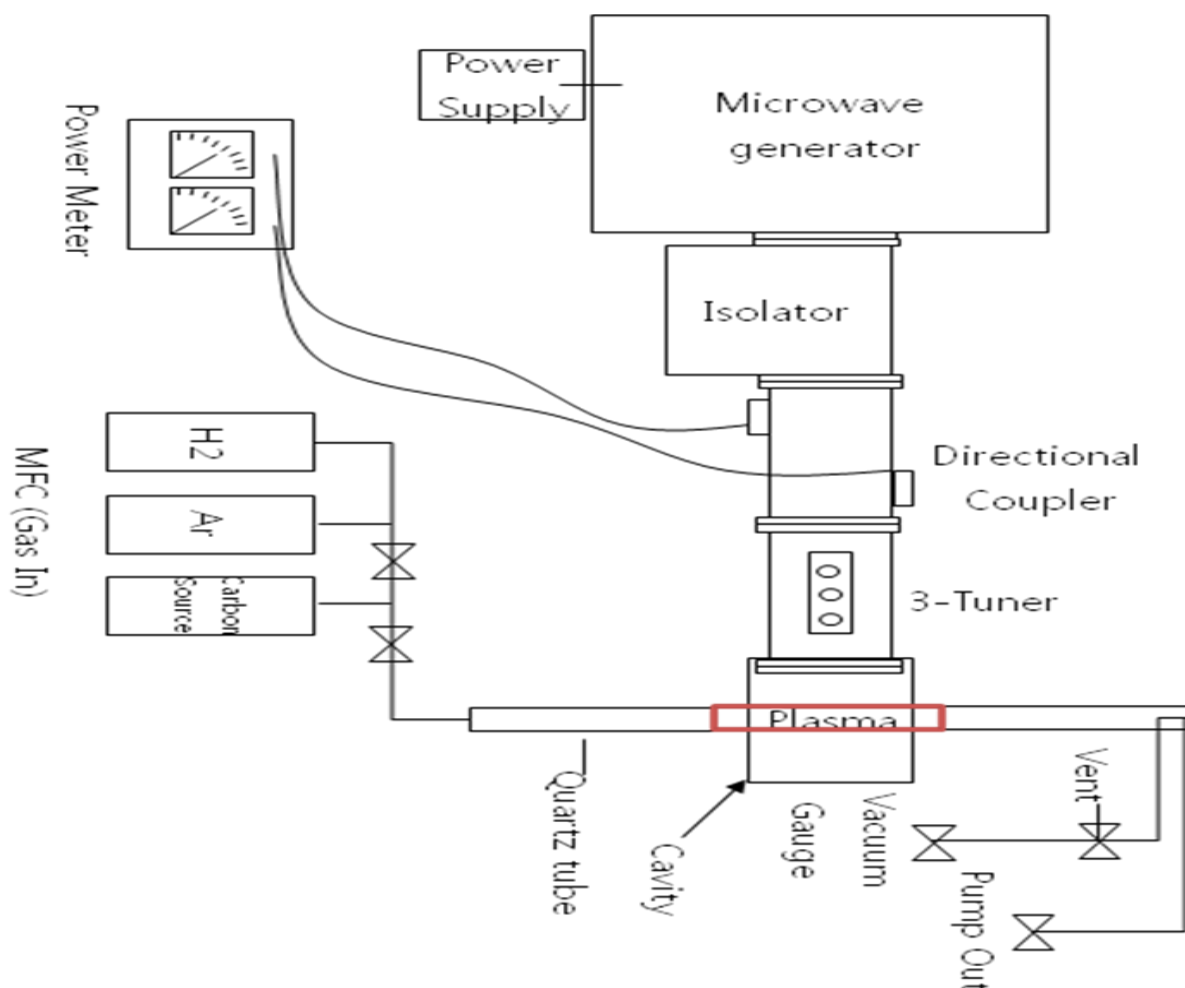

Figure 1. Schematic diagram of 3-tubular MPECVD system for nano-structured carbon films deposition.

Figure 1 shows the schematic diagram of the experimental set up used in this work. In this geometry no additional heater was needed for substrate heating. The substrate heating occurred automatically by microwave induction and plasma species collisions. The substrate temperature (Ts) was estimated by attaching a very fine ceramic thermocouple at the front side of the substrate. `Ts' was found to vary linearly from 300 ~ 450 ℃ at microwave powers 400 W during 10 min. There was no external heating and the increase in temperature on the site of deposition was an effect of plasma heating, which is dependent on a number of factors, such as microwave power, process pressure and gas composition. At a constant microwave power and pressure, Ts was found to increase rapidly with time in plasma, reaching a maximum in about 3 ~ 5 min and became constant thereafter. The plasma chamber was pumped down to a base pressure of 0.3×10^{-1} Tor by a rotary pump, and was then purged by H_2 gas up to a pressure of 0.50 Tor. An ultimate pressure of 0.50 Tor was set at H_2 flow rate of 80sccm. The Si substrates were pretreated in H_2 plasma for 10 min to achieve constant Ts at a given microwave power. H_2 gas was then replaced by C_2H_2 gas at a flow of 6 Standard Cubic Centimetre per Minute (sccm) to deposit carbon film maintaining total pressure at 0.80 Tor. The characterization of morphologies was achieved by means of SEM after deposition. The bonding structure of the deposited CNWs was studied by Raman spectroscopy with 514 nm Ar laser. A high-resolution transmission electron microscope (HR-TEM, JEOL, JEM 2000EX) was used to determine the atomic structure of the CNWs. The CNWs were removed from the substrates and dispersed onto TEM grids.

RESULTS

These petal - like carbon CNWs have large surface to volume ratio and sharp edges mostly normal to the substrate. Figure 2 show the SEM micrographs of carbon films.
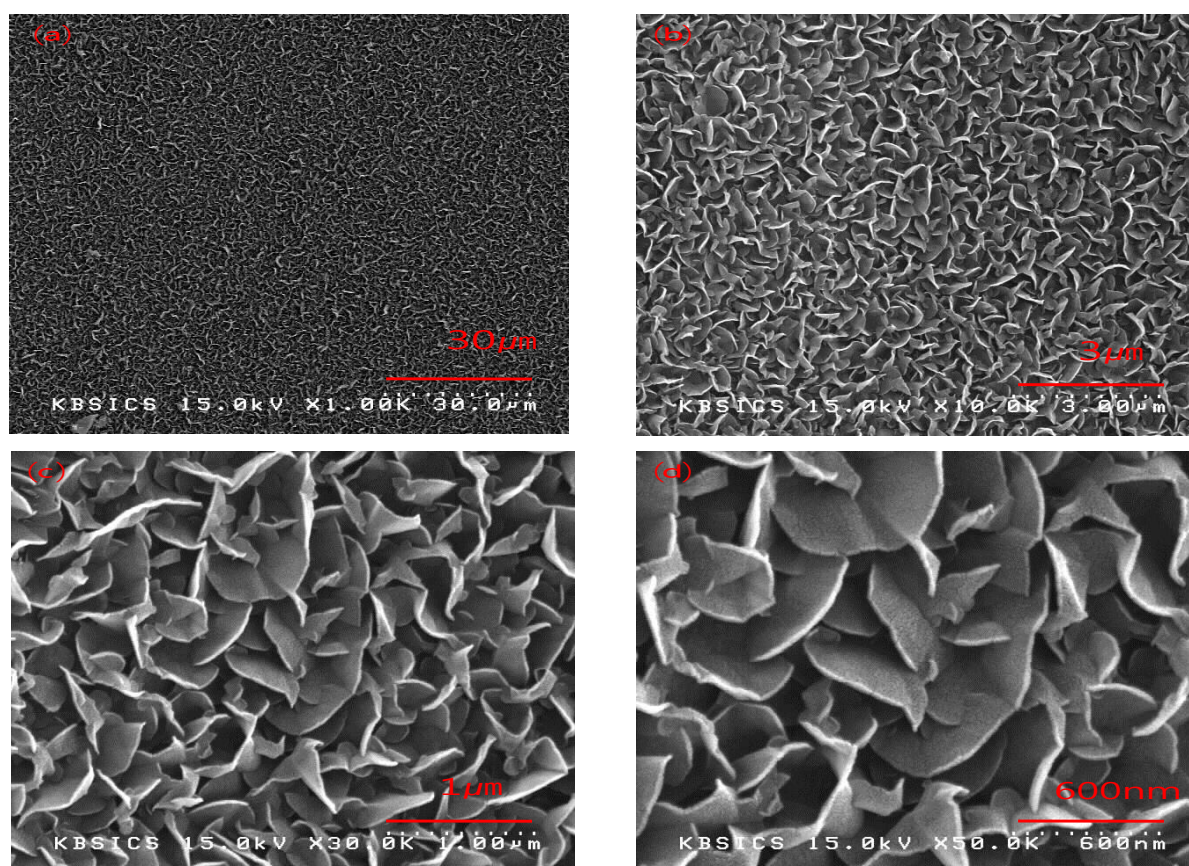

Fig. 2. SEM micrographs of carbon films deposits at microwave power of 400 W.
The petal-like pattern of carbon structures was formed on the substrate. It was found that these

carbon structures grew perpendicularly on the substrate and the shape was wall-like. The average side length of the unit structure is approximately 6 *µ*m and the thickness is about 100 nm. In order to investigate the growth mechanism of these petal-like sheets several films with varying deposition time were deposited at microwave power of 400 W keeping other parameters constant. The surface morphology of carbon films with varying time is given in Figure 3. (a), (b), (c).
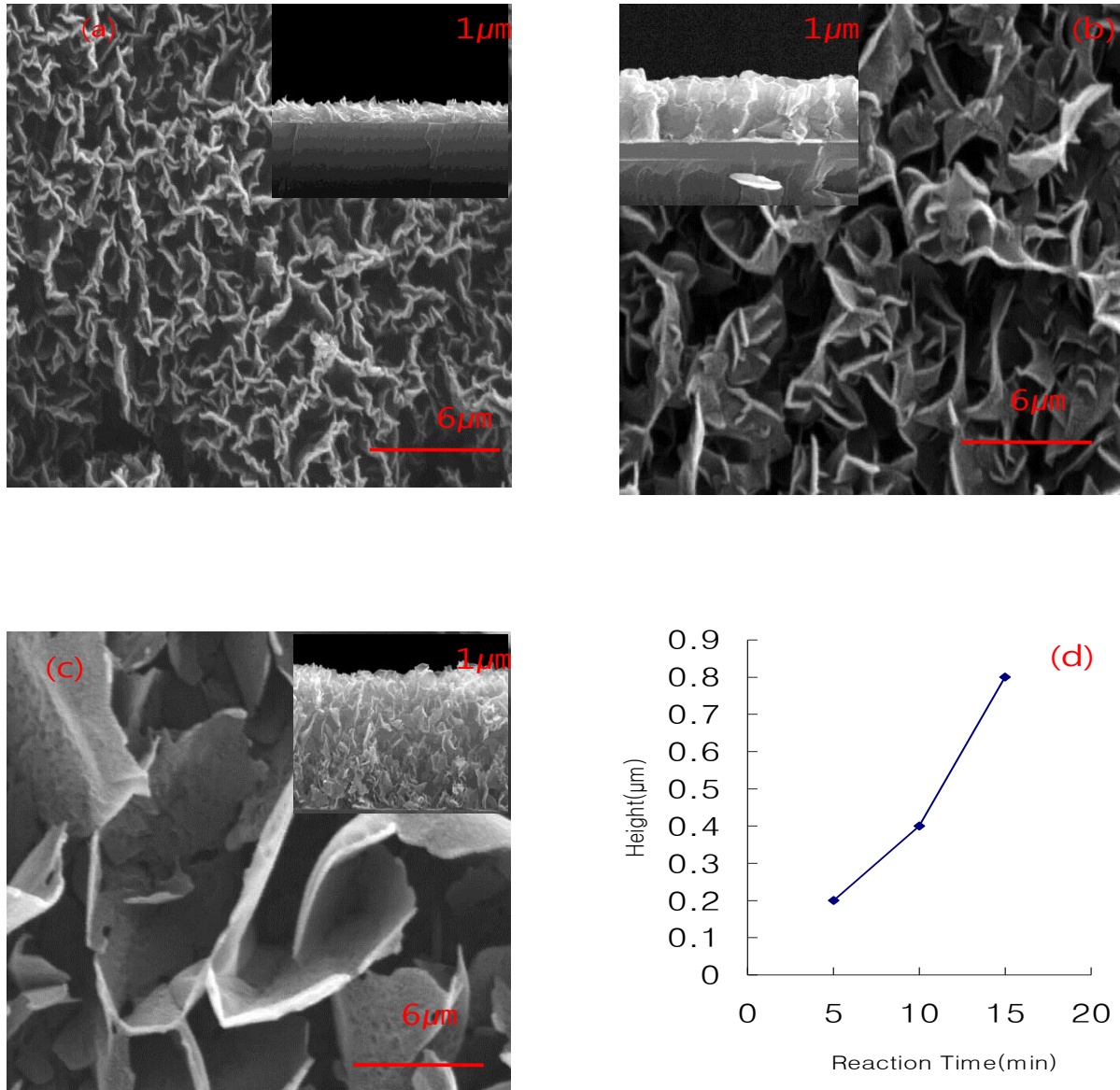

Fig. 3. SEM micrographs of the as-grown CNWs synthesized under different time of 5min(a), 10min(b), and 15min(c) respectively. Figure (d) shows the growth time dependence of the height of CNWs.

The top view and perspective view in Figure 3 shows CNWs at each growth stage. The SEM morphologies of the as-grown CNWs synthesized under different time of 5min, 10min, and 15min are shown in Figure 3(d) respectively. With increase in reaction times and hence Ts carbon nano-walls are found to grow, with sharp edges further aligned normal to the substrate surface. It is expected that increase in microwave power causes more ionization of the gas, which increases the density of plasma species of relatively higher energy. Increased nucleation of graphitic clusters is expected to occur and this leads to formation of carbon petals of

relatively smaller size and higher density at increased microwave power or Ts. It indicates the CNWs with a greater average apex angle and larger height diameters are deposited under a long reaction time in same condition. In other words, the higher concentration of C_2H_2 gas may lead to an increase of the lateral growth rate of CNWs to form a blunt apex angle. The results imply that the nanostructures of CNWs are determined essentially by the competition among etching rate of plasma species, the lateral growth rate and the upward deposition rate of carbon along the surface or through the interior of the catalysts. It is concluded that highly oriented CNWs are more likely to be formed under the appropriate concentration of carbon species in the plasma.

DISCUSSION

The Raman spectrum of the as-grown CNWs is shown in Figure 4. Raman spectroscopy gives rich microscopic information of the various all-carbon allotropes. In the case of graphitic carbon, Raman spectra present several characteristic bands: a G band near 1580 cm^{-1}, a D band near 1350 cm^{-1}.
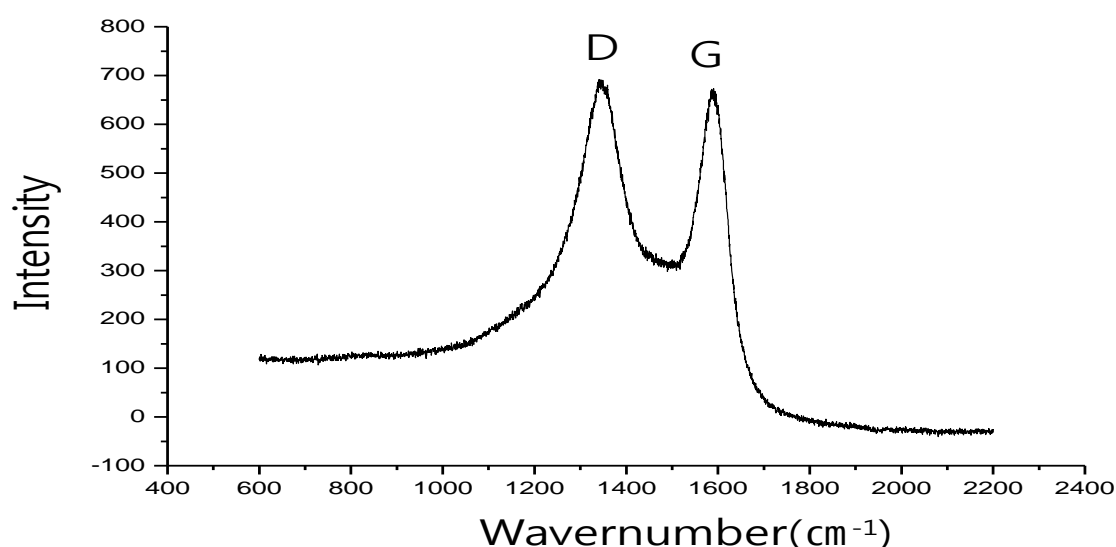

Figure 4. The Raman spectrum of the as-grown carbon nanowalls (CNW).
The peak position of the D band and G band are around 1334 and 1610 cm^{-1}, respectively, where the IG / ID ratio is ~ 0.82. Huang's group proposed that a shift of the E2gG mode from its normal value of 1580 to 1598 cm^{-1} is an indication of the existence of nano crystalline graphite or sp^2 clusters. The peak at 1334 cm^{-1} is assigned as A1g mode due to the presence of aromatic rings in disordered graphite rather than diamond peak at 1332 cm^{-1}. Therefore, the bonding structure of the as-grown CNWs can be considered as sp2 clusters in an amorphous carbon matrix.
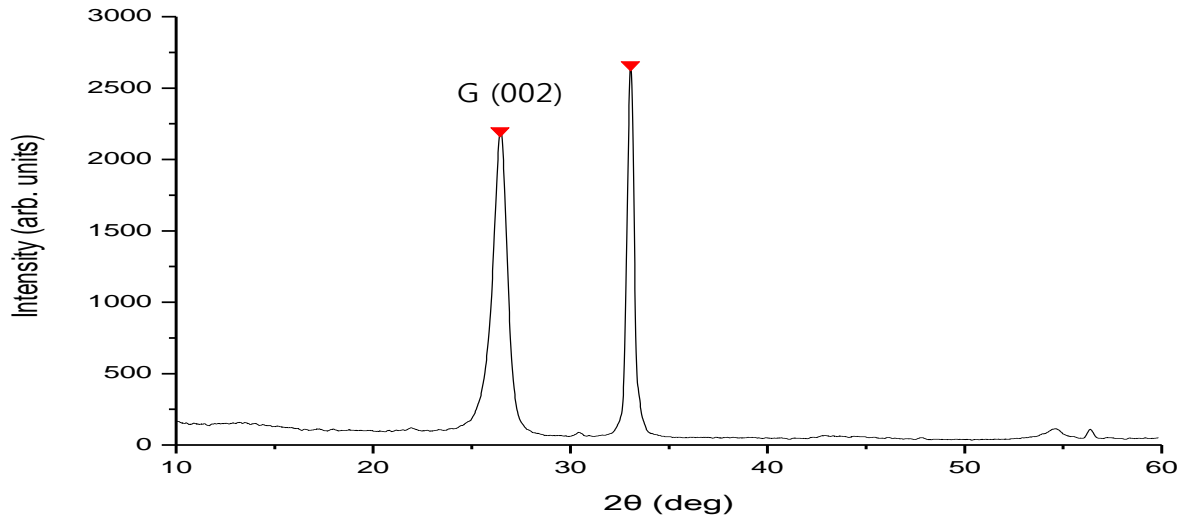
Figure 5. XRD of carbon nanowalls (CNW). The marked (↓) correspond to typical graphite phases of crystalline.

Figure 5 shows typical X-ray diffract gram of petal like carbon nanowalls. The peak at $2\theta \sim 26^{\circ}$ corresponds to the (002) plane of graphite. In addition to graphitic phase many small intensity peaks are also observed which correspond to face centered cubic phase of Si and its silicide. These peaks are marked and identified using standard data. This suggests that during the growth process some amount of Silicon silicide is formed by plasma ion bombardment.
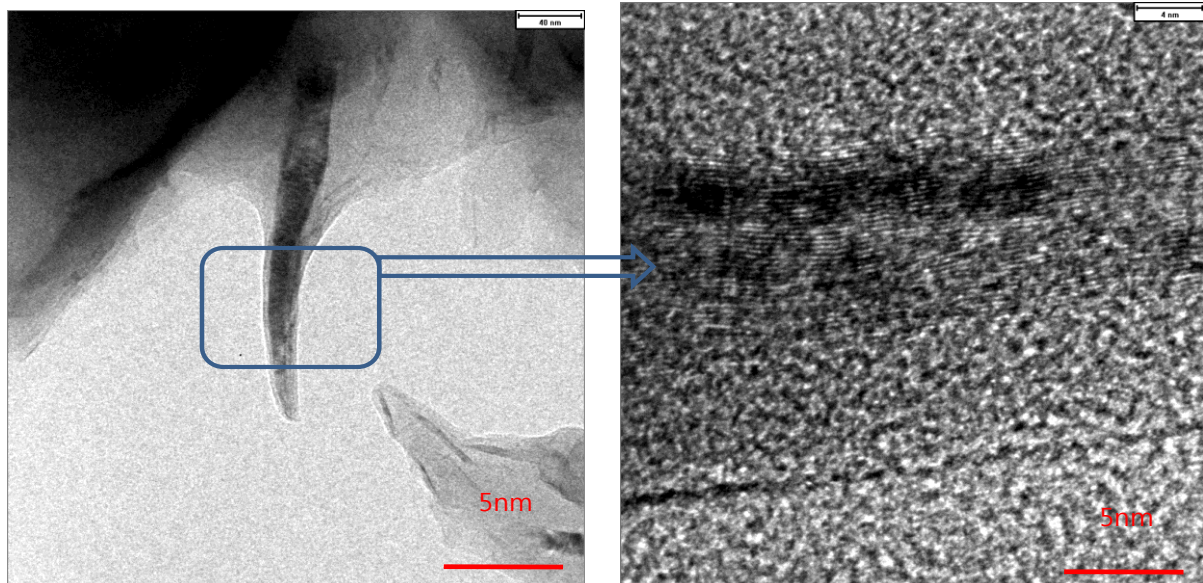

Figure 6. HR-TEM cross-section micrographs of Si (100) wafer surfaces (a). This images indicates the disordered crystalline structure with the lattice planes of graphite being visible (b).

The lattice images of graphite layers are observed in high resolution TEM micrographs of petal-like graphite sheets, as shown in Figure 6. Well-aligned graphite layers of 0.34 nm spacing were revealed in the graphite edge parallel to its axis direction, indicating that the original petal-like microstructure was preserved during MPECVD growth. The petal outgrowths appear to be 5 ~ 15 nm in width (see Figure 6-b), representing up to dozens of graphene layers. Neither significant disruption to the atomic arrangement of graphite layers nor disordered amorphous

regions are apparent in the petal interface. Therefore, the growth mechanism appears to involve sprouting and branching of petals from the superficial graphite fiber surface layers while maintaining the continuity of graphite structure from the fiber to petals.
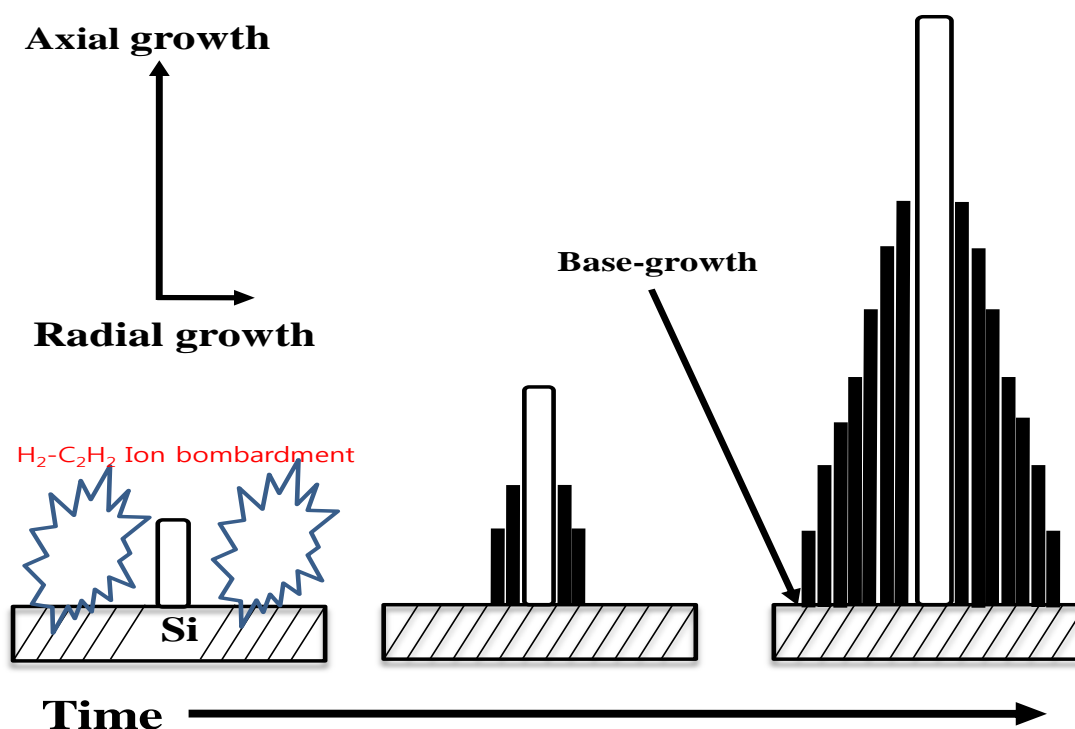

Figure 7. Mechanism of petal growth involves deposition of hydrocarbon radicals at or near the exposed surface graphene edges.

Figure 7 shows the likely mechanism of petal growth involves deposition of hydrocarbon radicals at or near the exposed surface graphene edges, which may be accentuated by the hydrogen - acetylene plasma treatment. The critical factor in determining the preference for diamond sp^3 lattice structures or graphene sp^2 structures upon deposition is the ratio of atomic hydrogen to acetylene in the plasma mixture. The present deposition pressure and plasma power conditions are similar to those that produce diamond growth, but the gas composition is more similar to that for carbon nanotube growth and is expected to be the most significant factor in determining the hydrogen : acetylene ratio. Further elucidation of the growth mechanism will require detailed plasma diagnostics experiments, which are ongoing.

CONCLUSIONS

The petal like carbon CNWs have been deposited for the first time by tubular MPECVD system on Si substrates in well-controlled manner without catalyst. The CNWs were nucleated at the fine-textured structure on the SiO_2 and grew with the increase in growth time. The reaction time is found to have a strong effect on the structure and morphology of these petal-like carbon CNWs. The growth mechanism of carbon films is found to be influenced by the surface morphology specific to the growth process. Improved alignment of the sharp edges of petals normal to the substrate, increased density, reduced size (geometrical enhancement factor) and solicitations between Si substrate and CNWs are found to be important factors contributing to the XRD characteristics of CNWs. The height of CNWs increased proportionally to the square root of time, in contrast to the previous studies, indicating a different growth mechanism. It is

also noted that an extremely high growth rate was achieved in this study.

ACKNOWLEDGEMENTS

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