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Innovative Variation in Morphological Characteristics of Carbon Nanowall Grown on Molybdenum Disulfide Interlayer

Chulsoo Kim¹, Kangmin Kim¹, Seokhun Kwon¹, Hyunil Kang¹, Byungyou Hong² and Wonseok Choi^{1*}

¹ Department of Electrical Engineering, Hanbat National University, Daejeon 34158, Republic of Korea; msdkcs1@gmail.com (C.K.); talk9797@naver.com (K.K.); kown1567@naver.com (S. K.); hikang@hanbat.ac.kr (H.K.)

² School of Electronic and Electrical Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea; byhong@skku.edu (B. H.)

* Correspondence: wschoi@hanbat.ac.kr

Abstract: Carbon, which exists in large quantities on Earth, is a material with interesting properties, and many studies have been conducted since the past. In particular, nano-sized carbon allotropes are called carbon nanomaterials, and many studies are currently underway. Among them, carbon nanowall (CNW) is a structure in which graphene of sp^2 bond is grown vertically, CNW have outstanding strength, can be highly electrically conducting or semiconducting, have a large specific surface area per unit mass. Electrical, chemical, physical properties of these CNW is modified by parameter such as surface density, height and thickness of it. Those have great effect on CNW and can be adjusted as growth interlayer. It was confirmed that the molybdenum disulfide (MoS_2) interlayer synthesized by radio frequency (RF) magnetron sputtering altered the morphological characteristics such as the shaped edge of the CNW, the pores diameter and density. Through these studies, we confirmed the effect of MoS_2 on the morphological characteristics of CNW. This opens the door to improving the performance of electrodes and devices.

Keywords: Carbon nanowall; Molybdenum disulfide; Interlayer; Morphological characteristics;

1. Introduction

Carbon-based materials have the advantages of metals, chemicals and ceramics. It has excellent strength and flexibility, is lightweight and has high electrical conductivity. In addition, it is a material used in various fields around the world because of its chemical stability. There are various carbon allotropes depending on hybridization bonding such as sp^2 , sp^3 , corresponding graphene, graphite, and diamond. Among them, CNW are the vertically oriented structures of graphene [1-4], and are promising candidates with very large specific surface areas [5]. Among carbon allotropes, CNW can be growth by plasma enhanced chemical vapor deposition (PECVD) at relatively low temperature [6], without catalysts can be grown on various substrates such as glass and polymer based substrate. In addition, CNW exhibit various physical properties depending to morphological characteristics. Morphological characteristics variation depending on several parameters such as reactant gas, power and working pressure. These results can be confirmed through diverse literatures, but there remain limited studies on morphological characteristics caused by interlayer. In this study, MoS_2 synthesized by RF-magnetron sputtering was used as an interlayer. MoS_2 , one of the representative materials of transition metal di chalcogenides (TMDC), is a two-dimensional material with excellent physicochemical properties [7,8]. It has been spotlighted as a semiconductor material replacing graphene, and a lot of research is being conducted around the world. In this paper, MoS_2 interlayer was synthesized on a glass substrate using RF-magnetron sputtering system to variation the morphological characteristics of CNW, and CNW grown on the MoS_2 interlayer showed interesting morphological characteristics. These results are attributed to the initial growth of

CNW in the MoS₂ crystal plane, it could also be due to van der Waals forces between surface of MoS₂ and graphene sheets [9].

2. Experimental method

2.1. Preparation of substrate

A glass substrate, which is amorphous SiO₂ was used. In the substrate cleaning process step, ultrasonically degreasing glass substrates in order trichloroethylene (TCE), acetone, methanol, deionized water (DI water) for 10 minutes.

2.2. MoS₂ Interlayer synthesis and annealing

MoS₂ interlayer was synthesized through a RF-magnetron sputtering system using a molybdenum disulfide (MoS₂, 99.9999%) 4-inch target (Table 1). Afterwards it was annealed in a vacuum chamber at 400°C and 10⁻⁶ Torr for 40min.

Table 1. Sputtering system parameters for MoS₂ interlayer synthesis.

Parameters	MoS ₂
RF Power	200 W
Base Pressure	10 ⁻⁶ Torr
Working Pressure	1.5 x 10 ⁻² Torr
Temperature	Room Temperature
Synthesis Time	10min

2.3. Growth of the Carbon Nanowall

The prepared MoS₂ samples was placed in the PECVD (2.45GHz microwave) chamber, a base vacuum was performed at 10⁻⁶ Torr for 24 hours. After 40 sccm hydrogen (H₂) gas and 20 sccm methane (CH₄) gas were injected into the chamber, a plasma was formed using 1300 W of 2.45 GHz microwave power. During the CNW growth process, the temperature and pressure were maintained at 600°C and 4 x 10⁻² Torr, respectively (Table 2).

Table 2. Process parameters of PECVD method for CNW growth.

Parameters	CNW
Microwave Power	1300 W
Reaction Gas	H ₂ 40 sccm and CH ₄ 20 sccm
Base pressure	10 ⁻⁶ Torr
Working Pressure	4 x 10 ⁻² Torr
Temperature	600°C
Growth Time	5, 10 and 15 minutes

2.4. Characterization and Analysis of Materials

In this study, the morphological characteristics of CNW were analyzed through field effect scanning electron microscopy (FE-SEM, HITACHI, Japan, S-4800). In addition, the intrinsic properties of carbon such as graphitization degree and defects of CNW were analyzed using Raman spectroscopy (HORIBA, Japan, LabRAM HR-800).

3. Results and discussion

3.1. Morphological characteristics of carbon nanowall

Figure 1 (a-1), (a-2) and (a-3) show the surface FE-SEM image of CNW grown on a glass substrate. The surface of CNW is serpentine and disordered regardless of the growth time. It is a morphological characteristic of primitive CNW and is defined by the zigzag-shaped edge [10], shown in Figure 1 (a-2). The reason is CNW grow anisotropically of

disordered due to defects in the graphene sheets that occur during the initial growth process [11]. Figure 1 (b-1), (b-2) and (b-3) show the surface FE-SEM image of CNW growth on the MoS₂ interlayer. In this case Figure 1 (b-1) and (b-2) provide sharp-edge shapes [12, 13] compared to CNW grown directly on the glass substrate. As the deposition time was increased to 15min, the Figure 1 (b-3) formed a rounded-edged shape and compared to Figure 1 (a-1), (a-2), and (a-3), the density was lower and the pores diameter between the edges increased. The CNW grown on the MoS₂ interlayer for 10 minutes showed the greatest deformation in the surface morphological characteristics of the existing CNW.

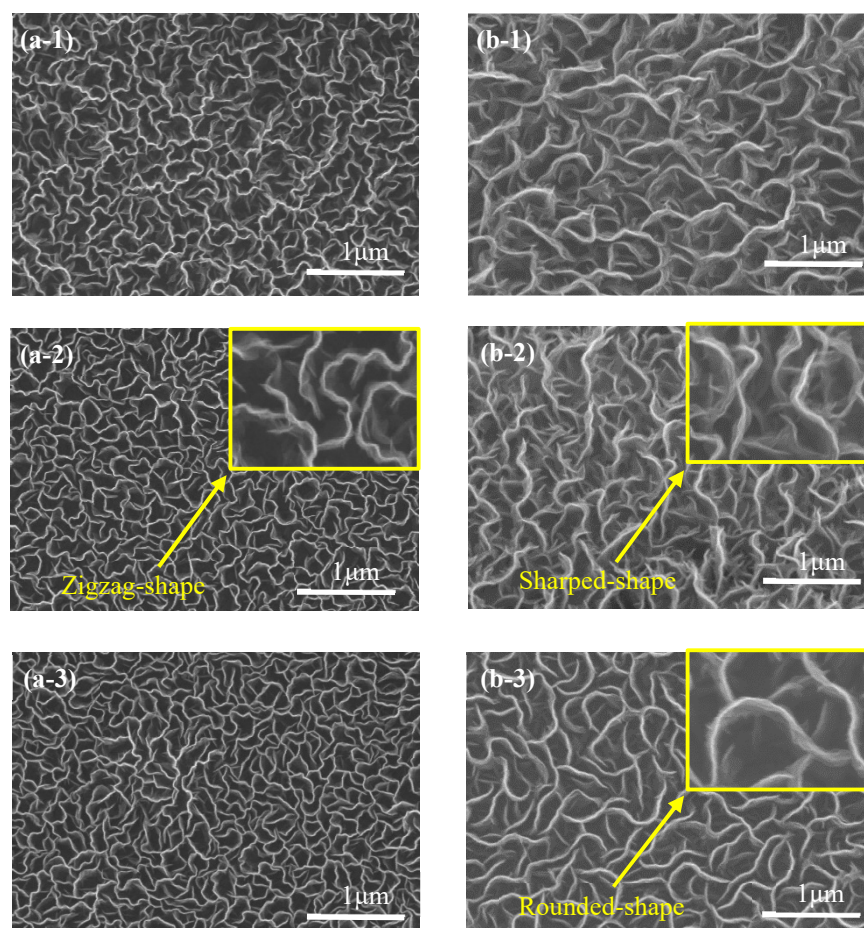


Figure 1. Shows the FE-SEM surface image of grown CNW on glass substrate; Growth time (a-1) 5min, (a-2) 10min and (a-3) 15min. Samples (b-1), (b-2) and (b-3) are FE-SEM surface images of CNW grown on the MoS₂ interlayer for 5min, 10min and 15min, respectively.

Cross-sectional FE-SEM images of CNW/MoS₂ samples synthesized on glass substrates for 10min each are shown in Figure 2. The height is 250 nm for MoS₂ and 750 nm for CNW. The vertically oriented MoS₂ sheet and graphene sheet regions have different diameters and densities. For this reason, we show a clearly interface between MoS₂ and CNW. Also due to the initial growth process of CNW occurring in macropores (< 50 nm) in the MoS₂ interlayer, they grow at a slower rate than native CNW (Figure 3). For a synthesis time of 10 minutes, respectively, CNW grown directly on a glass substrate grew to a height of about 1 μm, whereas the MoS₂ interlayer grew to 750 nm. The morphological characteristics of CNW are variation under the influence of the MoS₂ interlayer, which can be attributed to the interaction between sulfur or molybdenum atoms on the MoS₂ surface and carbon atoms in the graphene sheet. A graphene sheet with a low defect density is formed in the growth of the initial process by the van der Waals force generated at the interface and grows in a sharp shaped edge.

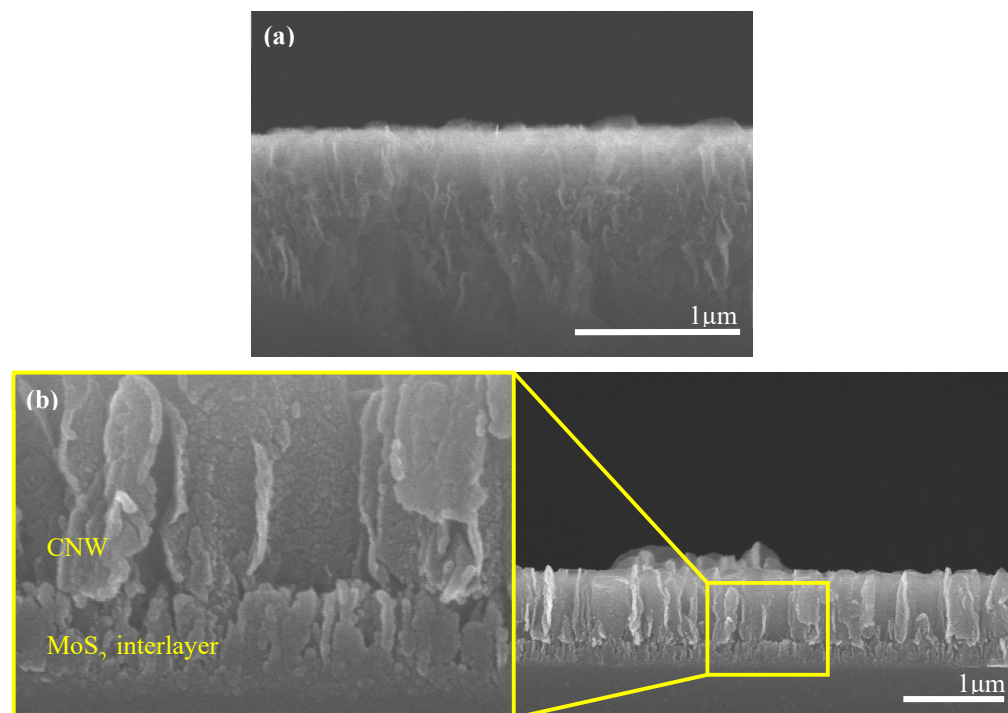


Figure 2. Cross-sectional FE-SEM image of CNW (a) CNW grown for 10min on a glass substrate, (b) CNW grown for 10min on MoS₂ interlayer and magnification image.

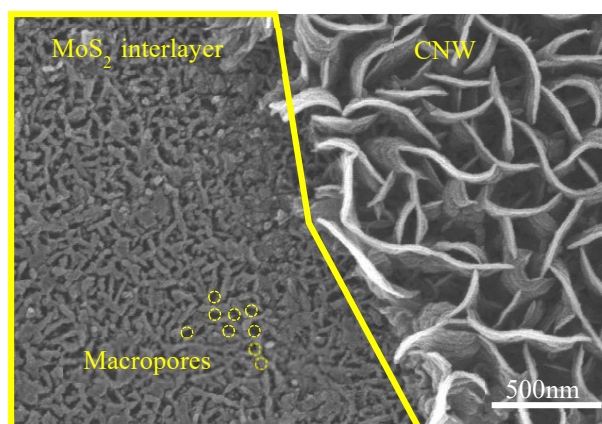


Figure 3. FE-SEM surface image including MoS₂, CNW and interfaces.

3.2. Raman spectra

Figure (4a) shows the results of Raman spectroscopy analysis before and after annealing of the MoS₂ interlayer. E_{12g} showing in-plane vibrational characteristics and A_{1g} showing interlayer vibrational characteristics were observed. Compared to pristine MoS₂, annealed MoS₂ exhibited a peak shift of approximately 11cm⁻¹ in E_{12g} mode from 351cm⁻¹ to 362cm⁻¹ [15]. The blue shift phenomenon is due to the increase of the van der Waals force between the MoS₂ interlayers during the annealing process. When the thickness of the interlayer decreases, the distance between E_{12g} and A_{1g} decreases [16]. The results of Raman spectrum analysis of CNW are shown in figure 4b. Defects in graphite or amorphous carbon cause a high intensity D-peak, it was observed at 1345 cm⁻¹ [17]. The presence of MoS₂ interlayer decreases the D-peak of CNW (figure 4c) Also, there is a G-peak at about 1592 cm⁻¹, and the increase in the intensity of this peak means that the graphitization degree is high, it is commonly found in all carbon materials [18].

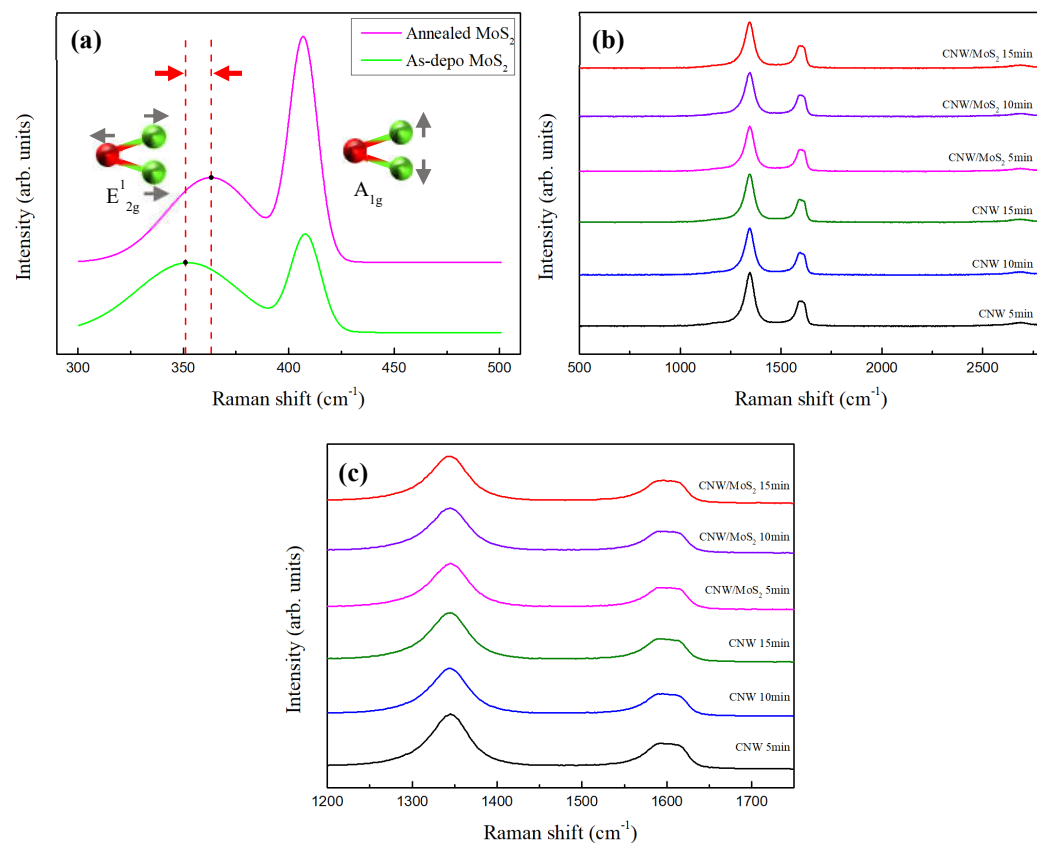


Figure 4. Raman spectra of CNW and MoS₂; (a) Raman spectroscopic analysis results before and after annealing of MoS₂ interlayer, (b) Raman spectroscopic analysis results of each CNW sample grown under various conditions, and (c) high resolution Raman spectrum of D and G peaks with enlarged entire Raman spectrum.

4. Conclusions

In summary, MoS₂, a transition metal dichalcogenide material, was successfully synthesized using the RF magnetron system, and CNW, a carbon allotrope, was grown using the PECVD method. In addition, the structural stability of MoS₂ was secured through heat treatment to lower the amorphous carbon ratio of CNW, and this result can be confirmed through the Raman spectrum. MoS₂ was used as an interlayer material for the morphological modification of CNW with a two-dimensional graphene sheet, the core subject of this study, and the surface density, pores diameter, and growth rate were changed. In this study, it was confirmed that the MoS₂ interlayer has a significant effect on the initial growth of CNW, and as a result, it is an innovative material that changes its morphological characteristics. Based on these results, it is expected to be applied to CNW/MoS₂ interlayer electrodes and devices to improve electrical, chemical and physical properties.

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