ANALYSIS OF CARBON NANOWALS PREPARED BY HOT FILAMENT CHEMICAL VAPOUR DEPOSITION

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Abstract

Carbon nanowalls (CNW) thin films are very promising for various electrochemical and energy storage applications. Its high surface area, porosity and good electrical conductivity make it an ideal electrode material for electrochemical sensors, supercapacitors and batteries or for ohmic contacts of GaN transistors. In this work, hot filament chemical vapour deposition (HFCVD) technique was used to grow CNW on silicon substrates using various gas flows of methane and hydrogen. Raman spectroscopy and SEM were used to perform the structural and morphology characterization of the prepared samples. The I_D / I_G ratio calculated from Raman spectra and its dependence on the CH_4 / H_2 ratio is described and discussed. We found that, the size and disorder of the multi-layer graphene structure of the deposited CNW thin films is strongly affected by the methane to hydrogen ratio.

Keywords: Carbon Nanowalls, HF CVD, Raman spectroscopy

1. INTRODUCTION

In the past few years, a great interest of researchers in different carbon nano-materials, such as graphene [1], diamond [2-7], boron doped diamond [8-12], fullerenes [13] and carbon nanotubes (CNT) [14-16] has arisen. Due to its nano- to micro- sized crystalline structure, carbon nanomaterials have interesting properties such as a large surface area and high aspect ratio and are a promising material for many applications [17-19]. The recent developments led to synthesis of carbon nanowalls (CNW), material with a multi-layered graphene structure [20]. CNW are intensively studied for use as electrodes for electrochemical sensors and energy storage [21]. For CNW production, different methods based on chemical vapour deposition (CVD) e.g. hot filament (HF CVD) [22], micro-wave (MW CVD), direct-current plasma enhanced (DC PECVD), etc. are used [23, 24]. However, correlation between the deposition conditions and the growth and structure is not sufficiently described yet. Furthermore, the correlation between obtained structure and application properties are not available.

2. EXPERIMENTAL

The depositions of CNW were performed using double bias HFCVD reactor described previously [25] on Si (100) substrates. The substrates were firstly cleaned in acetone, isopropyl and deionized water ultrasonic bath. The CNW were deposited for 30 minutes in CH_4/H_2 gas mixture, where the methane flow was constantly set up to 15 sccm and the hydrogen flow was varied from 0 to 300 sccm. Depositing pressure was 500 Pa. The gases were activated by five 0.7 mm thick tungsten filaments heated to about 2300 °C and substrate temperature was about 760 °C. Distance of the substrates from heated filaments was 10 mm. Characterization of the as deposited CNW thin films was done using SEM (JEOL 7500f) and μ-Raman spectroscopy (Dilor system working with He-Ne laser of 632.817 nm wavelength) at room temperature.

3. RESULT AND DISCUSSION

The SEM images of CNWs deposited with various methane-to-hydrogen ratios **Fig. 1** show homogenous layers of nanosized curled multi-layer graphene flakes with slightly different sizes. All of the experiments performed resulted into depositions of such curled, tenths of nanometers sized, more or less disordered and crystalline carbon nanowalls, instead of **Fig. 1d** with high hydrogen flow. The thickness of the as grown layers varied from 1.5 to 6 μm.

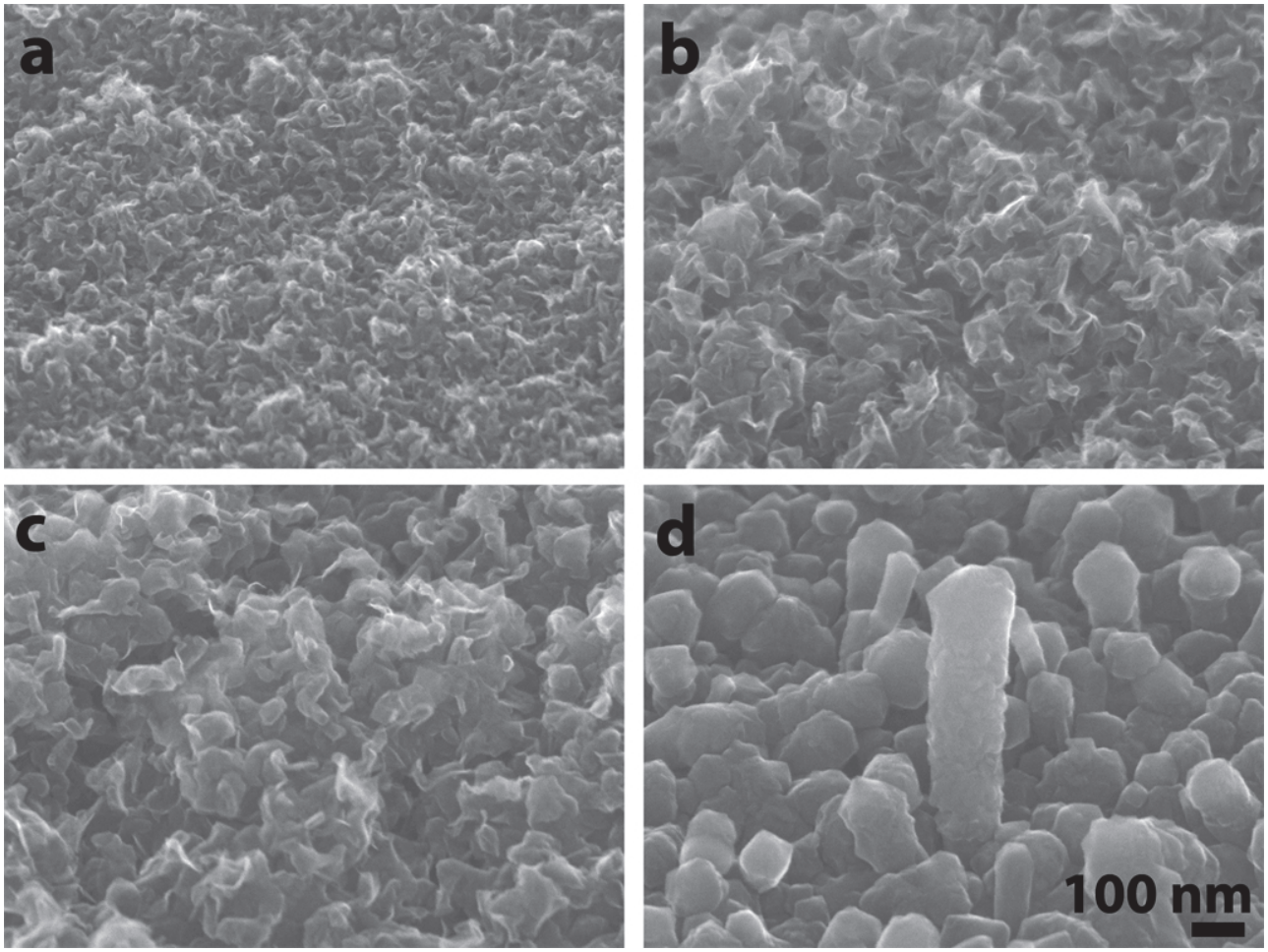

Fig. 1 SEM pictures of Carbon Nanowalls grown with different gas flow a) CH_4 / H_2 = 15 / 0, b) CH_4 / H_2 = 15 / 60, c) CH_4 / H_2 = 15 / 225, d) CH_4 / H_2 = 15 / 300 sccm

All of the deposited carbon nanostructure Raman spectra (**Fig. 2**) show bands which can be assigned to graphitic materials. The G-band at 1 580 cm^{-1} belongs to in-plane sp^2 vibrations of hexagonal carbon lattice, while the D and D' bands at 1 330 and 1 620 cm^{-1} represent disorder induced state of the graphitic planes. It describes the disorder state in the sp^2 hybridized material, created by finite size structure and the different orientations of the graphitic domains, defects, grain boundaries and edges [26, 27]. The strong D-band peak and D′-band peak suggest a more nanocrystalline structure and presence of graphene edges [26]. It is important to notice that the second order resonance is an evidence for a well ordered structure in the materials and is confirmed by 2D band (at 2 667 cm^{-1}), D+G band (2 920 cm^{-1}), 2D' band (3 240 cm^{-1}) [28]. The 2D-band is symmetric, but with a much larger full-width at half-maximum (FWHM) compared to 34 cm^{-1} for single-layer graphene. The broader 2D band is in agreement with multi-layer graphene structures without AB stacking of 3D graphite.

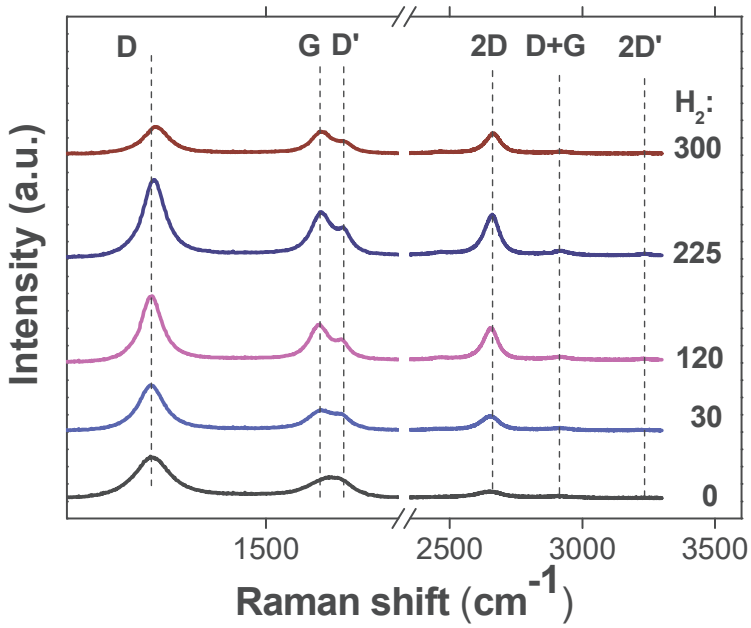

Fig. 2 Raman spectra of CNW deposited with different hydrogen flow (CH_4/H_2 - $15/H_2$)

During the deposition process, individual graphene sheets do not continue to grow vertically without defects. Instead many defects cause the termination and re-nucleation of graphene sheets making the grown graphene nanowalls to consist of many small graphene domains of tens of nanometers in size. Edges of these nanometer sized graphene domains break the hexagonal symmetry required for 2D-band Raman scattering. Therefore, the 2D-band intensity is lower and FWHM much higher than that of single layer graphene sheet. The disorder of such nanostructured CNW layer is high and the calculated I_D / I_G ratio is about 2. Fully grown nanowalls consist of curling graphene due to internal stress induced by defects in the multi layered graphene walls. Without the guidance of a flat surface like the growth of few-layer graphene on the copper surface, the growth of standing graphene nanowalls relies on diffusion of carbon species from 3D space. The incoming carbon species find favorable spots to nucleate new graphene, while defects cause graphene growth to terminate [29].

The degree of disorder becomes lower with increasing hydrogen flow. We think that, in case of high methane concentrations, the flow of the activated carbon species from the hot filament region towards the substrate is too high and the space around growing CNWs is saturated. Therefore, the re-nucleation and termination speed of graphene crystals is too high, resulting in a growth of nanosized curled CNWs. The dependence of the I_D / I_G ratio and there from calculated approximate crystallite size L_a of the CNW is showed in **Fig. 3.** Decreasing the CH_4 concentration in the gas mixture led to a growth of larger CNWs and to a lower I_D/I_G ratio. When the CH_4 concentration was higher, the G and D' maxima joined together to create a broad peak, which means less crystalline nature indicating amorphous content. On the other side, when the CH_4 / H_2 ratio reached 15 / 300 sccm and the relative amount of methane was too low, no CNW were grown indicating a very high etching speed of the sp^2 phase located on the CNW edges. Although this way deposited structures are also sp^2 bonded, graphene edges were not allowed to grow due to the continuous etching by atomic hydrogen. Thus we can assume that only by changing the methane-to-hydrogen ratio it is possible to grow CNW structures from small sized with higher amorphous phase to several times larger with much lower content of amorphous phase and better crystal quality. Hence, the degree of porosity of deposited CNW layers can be considered as easily controllable during the deposition process. This result can be taken as important for the application of CNW layers in electrochemistry, where for example catalytic metal nanoparticles very often have to be located

inside the thin film used as an electrode. With such a controllable porosity also the size and amount of nanoparticles might be influenced more accurately.

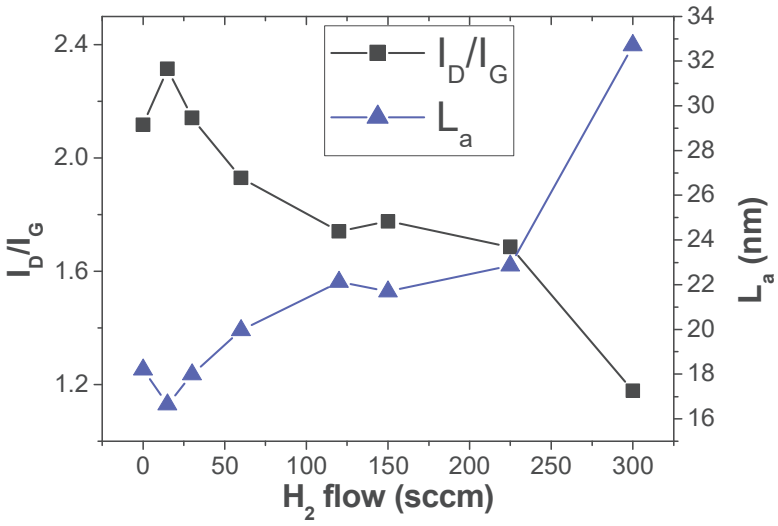

Fig. 3 Influence of hydrogen gas flow to I_D / I_G ratio and L_a size

4. CONCLUSION

Homogenous and well ordered CNW of different size and structure were deposited on Si substrates by HFCVD. Curled multi-layer graphene nanowalls properties were directly influenced by deposition conditions. The Raman spectroscopy suggested few- to multi- layer (2 to 10) graphene sheets structure. The calculated crystallites sizes of about tenth to hundreds of nanometres were in well agreement with the SEM observations. The level of disorder was significantly influenced by relative methane concentration. When the CH_4 concentration was too high, the G and D' Raman maxima joined together to create a broad peak, which means less crystalline nature indicating more amorphous content. On the other side, when the CH_4 / H_2 ratio was too high and the relative amount of methane was too low, no CNW were grown indicating a very high etching speed of the sp^2 phase located on the CNW edges. Obtained results indicate that only by changing the methane-to-hydrogen ratio it is possible to grow CNW structures from small sized with higher amorphous phase to several times larger with much lower content of amorphous phase and better crystal quality. Furthermore, the porosity of deposited CNW layers can be considered as easily controllable during the deposition process allowing better modification possibilities for applications in electrochemistry.

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