Is Aluminium Suitable Buffer Layer for Growth of Carbon Nanowalls?

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ABSTRACT

This work concentrates on the growth of carbon nanowalls (CNWs) using thermal chemical vapour deposition (T-CVD) technique on a glass substrate coated with Fe nanocatalyst and Al thin film as a buffer layer. A combination of $C_2H_2/NH_3/H_2$ renders the growth of carbon nanostructures at atmospheric pressure. Parameters affecting the growth of the CNWs such as C_2H_2 flow ratio, deposition time, and temperature are investigated. Surface morphologies of thin films are observed using AFM technique, while the thicknesses were measured by RBS technique. The samples utilized are characterized by the SEM, TEM, and Raman spectroscopy techniques. Results show forming some of maze like carbon nanostructures TCVD employing $C_2H_2/NH_3/H_2$ (20:80:100 sccm) for 45 minutes at atmospheric pressure, and 600°C substrate temperature. One of the important conclusions is that the an increase of the temperature from 600°C to 700°C causes the formation of the CNTs and the CNWs on the substrate.

***Keywords*:** carbon nanowalls, glass substrate, thermal CVD, Fe nanocatalyst, Al buffer layer

1 INTRODUCTION

Self-assembled carbon nanostructures like carbon nanotubes (CNTs) [1] and nanofibers [2] have attracted much attention for several applications, such as gas storage, membranes for electrochemical energy storage, and field emitters [3,4]. In addition, two-dimensional graphitic carbon structures, commonly referred to as carbon nanowalls (CNWs) or nanoflakes, are found attractive both as far as their structures, and their applications due to their high surface to volume ratios. Moreover, these structures have a great potential to act as metallic clusters supporting elements for electrochemical fuel cells. The morphologies of the metallic clusters supports have much effect on the chemical activity of the metallic clusters themselves [5]. Also, the carbon nanowalls very sharp and thin edges being perpendicular to the substrates can act as field emitters [6]. In another work, a transmission electron microscopy study has revealed that the CNWs consisting of a few graphene sheets were stacked together, like thin graphite flakes [7]. Wu, et al. [8] have shown that CNWs can grow vertically on a substrate with catalyst using a microwave plasma enhanced chemical vapor deposition (PE-CVD). Hiramatsu, et al. [9] have shown that CNWs can grow vertically on a substrate without catalyst using radio-frequency (rf) PECVD with a H radical injection. Recently, Escobar and co-workers [10] reported the effects of acetylene pressure on nanotubes characteristics by CVD on Fe nano-particles at 180 torr. Very recently, Alizadeh et al. [11] and ghoranneviss et al. [12] have reported the growth of CNWs on a Fe catalyzed substrate using thermal chemical vapor deposition (TCVD) in atmospheric pressure.

In this paper, a glass substrate is coated with Fe nanocatalyst and Al thin film as a buffer layer by low temperature plasma. Carbon nanostructures (two-dimensional carbon nanostructures and CNTs) are grown on the Fe-Al-glass substrate by TCVD using acetylene (C_2H_2) as a carbon sources, and a number of diluting gases such as hydrogen (H_2) and ammonia (NH_3). Effective parameters such as the C_2H_2 flow ratios, time, and CNWs temperature growth are to be studied. The samples are to be analyzed for characterization of the surface morphology and the roughness parameters of the substrate, alignments, distributions, and carbon nanostructures types. These characters are measured by atomic force microscopy (AFM), Rutherford back scattering (RBS) spectrometer, scanning electron microscope (SEM), Raman spectroscopy and transmission electron microscopy (TEM).

2 EXPERIMENTAL SET UP

2.1 Substrate Preparations

The glass substrate is coated with Al thin film as a buffer layer in first step, and then Fe nanocatalyst coated on the Al buffer layer in second step. Al thin film with 1 nm thickness and Fe nanocatalyst with 2 nm thicknesses were deposited on the microscopic glass slides (5 mm × 5 mm × 0.9 mm) by low temperature plasma. The instrument used in this experiment was a direct current magnetron sputtering (DC-MS) device. This instrument consisted of a cylindrical glass tube and two Al or Fe co-axial cylinders used as a cathode (the inner one: 30 mm diameter and 200 mm length) and an anode (the outer one: 100 mm diameter and 200 mm length) in its chamber. Argon (Ar) was selected as a sputtering gas, and the operation pressure was set at 0.03 torr. The substrates were cleaned by ultrasonic vibration with acetone, ethanol, and deionized water to remove all the contaminants. For Al and Fe Coating, a uniform magnetic field of 400 Gauss was induced from the outside. The applied voltage between the anode and the

cathode was about 900V which produced a 120mA current. The microscope glass slide used as a substrate was fixed on the anode. The distance between the target and the substrate was measured to be about 30mm. The surface morphologies of the films obtained in this manner, were observed using the AFM (Auto probe PC, Park Scientific Instrument, USA). Film thickness was measured using the RBS technique, using He^+ ion beam of 10 µm in diameter with 2.0 MeV energy. A typical RBS spectrum of Fe thin film is given in Fig. 1.

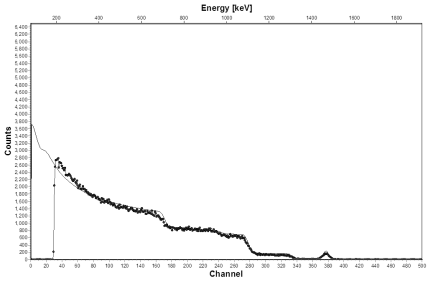

Fig.1. Rutherford back scattering (RBS) curve shows that that the thicknesses of Fe thin film coated on glass substrate is 2 nm.

2.2 Growth of Carbon Nanostructures

A thermal chemical vapour deposition (T-CVD) system was used in this study for growing the carbon nanostructures. This system consists of a horizontal quartz tube used as a reaction chamber, and a furnace surrounding the reaction chamber. The Fe-Al-glass substrate was placed on the ceramic boat, and was pushed into the reaction chamber at the centre of the furnace. To avoid the catalyst oxidation, argon (Ar) gas at 200 standard cubic centimetres per minute (sccm) was fed into the chamber of the CVD, and the chamber temperature was increased to 350°C. For etching the substrate, the Ar gas valve was closed, and the H_2 gas valve was opened (100 sccm) until the temperature was reached 500 ºC. The time taken for the etching was 30 minutes. A combination of $C_2H_2/NH_3/H_2$ with 20:80:100 (sccm) flow ratios were fed into the reaction chamber. The reaction time and the temperature for the growth were 45 minutes, and 600°C, respectively. In the other experiments, the conditions were changed by changing the gas flow, the time, and the temperature from 20 to 48 sccm, 45 to 60 minutes, and 600ºC to 700ºC, respectively, one change at a time. The carbon nanostructures obtained using this technique were analyzed using the SEM (XL30, 15-30.kV, Philips Company), and the Raman spectroscopy (Thermo Nicolet Crop. Madison, Wisconsin 53711, USA with 1064 nm wave length). TEM (CM120, 120 kV, Philips Company, with a W cathode).

3 RESULTS AND DISCUSSIONS

Surface morphology of the Fe nanolayer on the Al-glass was observed using the AFM, and the configuration is shown in Fig.2. The average roughness of the Fe-glass is measured to be 2.64Å.

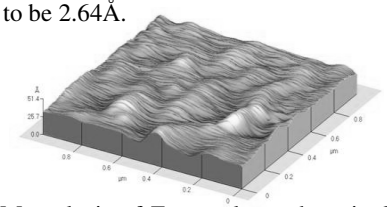

Fig.2. AFM analysis of Fe nanolayer deposited on the Al-glass substrate by D.C magnetron sputtering.

The SEM micrographs in Fig. 3 show the morphologies of the carbon nanostructures grown on the Fe nanocatalyst coated on the Al-glass substrate. Maze like carbon nanostructures were obtained by the T-CVD by applying the $C_2H_2/NH_3/H_2$ mixture (20:80:100 sccm) for 45 minutes at atmospheric pressure, and at 600°C. Fig. 3(a) shows the SEM image of these nanostructures. The image shows that the two-dimensional carbon nanosheets were grown vertically on the substrate. The thin two-dimensional carbon nanosheets formed have thicknesses of less than 28nm. Fig 3(b) shows the SEM image of the high density no uniform carbon nanostructures grown by TCVD employing the $C_2H_2/NH_3/H_2$ (20:80:100 sccm) mixture for 60 minutes at atmospheric pressure and 600°C substrate temperature. Fig 3(c) shows that an increasing in the C_2H_2 flow rate caused to grown high density no uniform carbon nanostructures on the substrate, too. Fig. 3 (d) shows the SEM image of the CNTs and CNWs obtained on the substrate by the TCVD employing $C_2H_2/NH_3/H_2$ (20:80:100 sccm) mixture for 45 minutes at atmospheric pressure and 700°C temperature. This SEM image shows that the CNTs with 61nm in diameter were formed on the CNWs with 24nm in thicknesses. Growing of the CNWs in this manner has randomly orientation. However, average of distances between the adjacent CNWs were grown, by TCVD employing the $C_2H_2/NH_3/H_2$ (20:80:100 sccm) mixture for 45 minutes at atmospheric pressure and 700°C substrate temperature, is 86 nm (fig. 3d). The limitations of the process for growing CNWs on a Fe coated Al-glass were analyzed through some parameter studies. The parameters in this case were temperature, time, and gas flow ratio. The results of these parameters studies show that the best CNWs growth condition takes place at 700°C, using $C_2H_2/NH_3/H_2$ flow ratios of 20:80:100, and a 45 minutes period. Since the experimental runs occur at atmospheric pressure, to minimize the unwanted reactions and ionization of the species included in the process, a high flow rate of Ar gas is fed into the reaction chamber. In other hand, the results of these parameters studies show that the maze like carbon nanostructures were grown by using $C_2H_2/NH_3/H_2$ flow ratios of 20:80:100, at 600°C temperature, and a 45 minutes growth time. One of important characterizations of ideal CNWs is high ratio for length/thicknesses ratio. So, investigation of this amount show that, the length/thicknesses ratio for CNWs were grown, by TCVD employing the $C_2H_2/NH_3/H_2$ (20:80:100 sccm) mixture for

45 minutes at atmospheric pressure and 700°C substrate temperature, is about 14. These results show that, increasing the substrate temperature from 600 to 700°C causes to obtain the better structures of the CNWs in this manner.

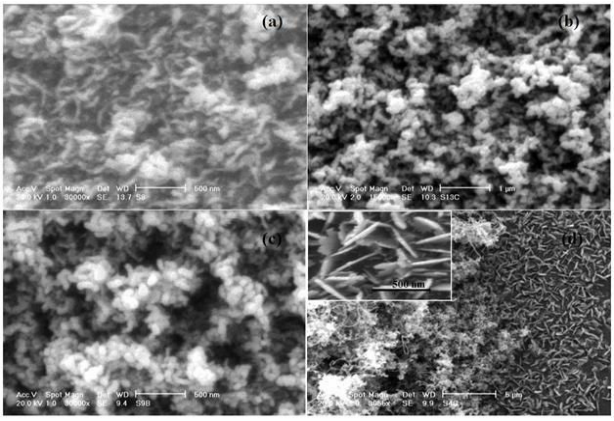

Fig.3. SEM images of the carbon nanostructures grown on the glass substrate coated with the Fe nanocatalyst on the Al buffer layer with conditions: (a) $C_2H_2/NH_3/H_2$ (20:80:100 sccm) for 45min. and 600°C; (b) 60 min., (c) 48 sccm, and (d) 700°C.

The Raman spectra of the carbon nanostructures grown on the Fe glass substrate coated with Fe nanocatalyst on the Al nanolayer as a buffer layer, for two conditions are shown in Fig. 5. Generally, for the carbon nanowalls, three Raman bands can be identified. The D-band around 1320 cm^{-1}, the G-band around 1580 cm^{-1}, and the D'-band around 1610 cm^{-1}. As shown in Fig. 5(a), the Raman spectrums for the two-dimensional carbon nanosheets were found to have a G-band peak at 1580 cm^{-1}, indicating the formation of a graphitized structure and a D-band peak at 1310 cm^{-1}, corresponding to the disorder-induced phonon mode. The G and D peaks are comparable in their intensities. It should be noted that the G-band peak is accompanied by a shoulder peak at 1610 cm^{-1} (D'-band). This shoulder peak is associated with the finite-size graphite crystals [13]. The strong G-band peak suggests a more nanocrystal configuration structure, and a presence of graphene edges and defects such as distortion, voids, and strains in the graphitic lattices which are among the prevalent features of the CNWs. The crystallite size "*La"* stems in I_D/ I_G intensity ratio. The empirical formula "*La*=44/ (I_D/ I_G)" has been successfully used for Raman spectra taken with the excitation energies around 514.5 nm [14], although the I_D/ I_G intensity ratio strictly depends on the Raman excitation energy [15]. Therefore, the above formula was also employed for Raman spectra with 1064 nm excitation energy in the present experiments. From these estimations, it is found that the average crystallite size "*La"* for the CNWs obtained in this study is 11.67 Å. Fig. 5(b) shows three Raman bands. The D-band is around 1320 cm^{-1}, the G-band is around 1580 cm^{-1}, and the D'-band is around 1607 cm^{-1}. These images show that the carbon nanowalls (CNWs) were grown vertically on the substrate. With increasing the temperature to 700°C CNWs were grown completely. The average crystallite size, "*La"*, in the CNWs were obtained in the present experiment is 49.43 Å. Also, fig. 5(b) shows the Raman spectrums of the CNTs were grown on the CNWs. In this present work it is found that an optimum $NH_3/H_2/C_2H_2$ gas ratio is 4:5:1. The experimental runs indicate that the presence of a catalyst on a buffer layer is a necessary condition for the growth, since no CNWs could be synthesized in the absence of a Fe catalyst and Al buffer layer. In this work a qualitative analysis of the carbon coating is performed with Raman spectroscopy. Each spectrum shows three characteristic carbon bands, i.e., the disorder induced the D-band around 1350 cm^{-1}, the G-band around 1580 cm^{-1} (that is related to in-plane sp^2 vibrations), and the D`-band around 1610 cm^{-1} [15-17]. For a qualitative analysis of the graphite-like structures, the intensity ratio of the D-band is compared with that of the G-band. This ratio here is denoted as the R-value, "$R = I_D/I_G$" [16]. CNWs usually suffer from defects, and are well-known for their relatively large R-values, exceeding unity, while pure CNTs and highly ordered graphite can have R-values close to zero [16,17]. The Raman spectra of the CNWs showed the R = 3.77 and 0.89 for Figures 3a and 3d, respectively. These results indicate that the CNWs are somewhat more in order with respect to their sp^2 structures. In this present work the equation "*La*=44/ (I_D/ I_G)" [13] is implemented to investigate the crystallite size of the CNWs.

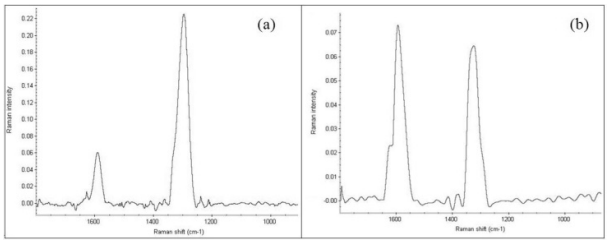

Fig.4. Raman spectrum of the carbon nanostructures grown on the glass substrate coated with the Fe nanocatalyst on the Al buffer layer with conditions: (a) $C_2H_2/NH_3/H_2$ (20:80:100 sccm) for 45min. (b) 700°C.

These results show that the increase of temperature from 600°C to 700°C causes formation of the CNTs and the CNWs on the substrate. Fig. 3(d) shows the SEM image of the CNTs with 61nm in diameter and CNWs obtained on the substrate. These CNTs characterized by TEM. For the TEM studies, a small amount of the CNTs was put down on a grid. Both the morphologies and the CNTs size are estimated by the TEM micrographs. Fig. 6 shows TEM micrograph of CNTs obtained by TCVD on the glass substrate at 700ºC temperature. As it can be seen, the CNTs exhibit a non uniform diameters and high length/diameter ratios. The various CNTs show in the TEM micrograph with different diameters multi wall carbon

nanotubes (MWCNTs). These CNTs have helical configuration. Length and minimum diameter of the CNTs are amount 550 nm and 9 nm, respectively. Maximum diameter of the MWCNTs is 25 nm. Some of metal catalyst particles detected that encapsulated in the nanotube and/or at the tip of the nanotubes.

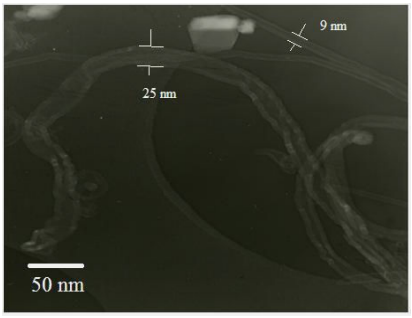

Fig.6. TEM image of CNTs were grown by increasing the growth temperature from 600ºC to 700ºC. This image shows that the CNTs are collective of MWCNTs and helical configuration. Minimum diameter of CNTs is 9 nm and maximum diameter is 25 nm.

4 CONCLUSIONS

In this paper, the carbon nanowalls, and carbon nanotubes were synthesized by the T-CVD system at atmospheric pressure. These carbon nanostructures were produced on the glass where Fe thin film as the magnetic catalyst and Al thin film as the buffer layer were deposited by a DC magnetron sputtering. C_2H_2 was used as carbon sources. H_2 and NH_3 were applied as diluting gases, and the following concluding remarks were reached:

a) The SEM characterization procedure shows that the two-dimensional carbon nanosheets were grown on the Fe catalyst coated on the Al buffer layer.
b) Increases in the C_2H_2 flow ratio, and time duration of the reaction cause the producing no uniform carbon nanostructures on the substrate.
c) An increase of the temperature from 600°C to 700°C causes an increase in the crystallite size (*La*) of the CNWs and the formation of the CNTs on the substrate.

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