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Effects of Sputtering Gas and Metallic Thin Film on the Growth of Carbon Nanostructures

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Abstract: Effects of different sputtering gases and metallic thin films on the growth of carbon-based nanostructures (CNSs) have been studied in detail. Aligned carbon nanowalls (CNWs) and multi-walled carbon nanotubes (MWCNTs) were synthesized on glass substrate at a low temperature in atmospheric pressure via thermal chemical vapor deposition (TCVD) techniques. The Iron (Fe) and Aluminum (Al) thin film is prepared using DC Magnetron Sputtering method with certain voltage, time and optimized deposition pressure. Surface morphologies of the films have been studied by atomic force microscopic (AFM).When the sputtering gas convert from Argon (Ar) to Nitrogen (N_2), the deposited carbon material changes from carbon nanowalls (CNWs) to multi-walled carbon nanotubes (MWCNTs). Additionally, the density of carbon nanostructures has changed by different metallic thin film. Acetylene (C_2H_2) as a hydrocarbonic gas with Ammonia as a dilution gas was applied during the activation and deposition process.

Key words: Carbon nanotubes · Carbon nanowalls · Sputtering · Thin film · Chemical vapor deposition

INTRODUCTION

Many considerable developments in the field of carbon-based nanostructures (CNSs) have been subjected of a great interest in research. The quest to reduce the size of electronic devices and mechanical devices provides the main driving force behind the scientific research and technological advancement in nanotechnology. Carbon nanotubes (CNTs) are promising candidates for emitter materials of cold cathodes due to their unique properties, such as high aspect ratio, high mechanical strength, chemical inertness and large current capability [1-3]. Therefore, field emission display (FEDs) based on CNTs have attracted much attention in recent years [4]. For FEDs using normal glass is cost effective. In recent years, using anodic porous alumina (APA) templates, a series of carbon nanotube (CNT) arrays on different substrates have been synthesized because of their promising applications in field-emission (FE) devices and nanoelectronics [5]. The APA template has highly ordered pore arrangement, controllable pore diameter and channel length and fine insulating property [6-8]. These are all very useful for applications of CNT arrays in nanoelectronics and nanodevices. On the other hand, the growth of carbon nanotube arrays using iron catalyst embedded in porous silica were reported [9-11]. Several methods have been well developed for preparing CNTs on glass substrates such as laser ablation [12], arc discharge [13] and chemical vapour deposition (CVD) [14]. In recent years, different chemical vapour deposition methods such as hot filament chemical vapour deposition (HF CVD), TCVD, Plasma enhanced chemical vapour deposition (PECVD) for synthesize of carbon nano structures have been developed. The CVD method allows the alignment, the density and the diameter of CNTs to be controlled. Thermal CVD process is known to be a most effective way for scale-up fabrication of vacuum microelectronic devices [15]. In particular, CVD under atmospheric pressure will not require sophisticated vacuum and control systems and therefore be much more cost effective. We investigate the effect of single layer and multi layers of thin film that deposited on microscopic normal glass slides with two different sputtering gases by means of DC Magnetron Sputtering method in certain voltage, time and optimized

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deposition pressure. Synthesize of aligned Carbon nanowalls and carbon nanotubes in atmospheric pressure, low temperature and using normal glass as a substrate are three advantages of this work. The growth behaviour of CNTs and CNWs on glass is not only influenced by the growth temperature, but is also highly dependent on the catalyst layers. The morphologies and the micro structures of the synthesized CNTs and CNWs were analyzed by the Scanning Electron Microscope (Philips instrument) and Raman Spectroscopy (Nicolet).Surface morphology of thin films and roughness parameters were observed by using atomic force microscopy (Autoprobi cp, Park Scientific Instrument).

Experimental Details

Substrate Preparation: The Iron (Fe) and Aluminium (Al) were prepared in the forms of single layer and multi layers thin film, which were formed using the general sputtering method, respectively. In the single layer of thin film, Iron and Aluminium were sputtered on microscopic normal glass slides (5mm×5mm×1.5mm) separately and the designed composition of the catalyst was controlled by adjusting the DC power source. In the mono layer, Iron and Aluminium were sputtered in certain voltage, time and optimized deposition pressure with Argon and Nitrogen as a sputtering gas. For multilayer thin films Fe and Al were sputtered in glass respectively. The instrument used in this experiment was dc cylindrical magnetron sputtering system; consist of a cylindrical glass tube two aluminium or iron coaxial cylinders(depends on coating layer) were made as cathode (inner one) and anode (outer one) in this chamber. Cylinders were 100 mm and 30 mm in diameter and 200 mm in length. Before sputtering, the glasses were cleaned by 3-step ultrasonic vibration acetone, ethanol and deionised water for 10 min independently, to remove all contaminate and degreased. We apply potential voltage of 2kv and electric current of 2A. The base pressure and operation were 10^{-5} and 10^{-2} respectively for sputtering iron and aluminium. For investigation of the multi layers effect, we sputtered aluminium on the glass/Iron substrate in the same condition. Moreover, we altered argon as a sputtering gas to nitrogen for considering the effect of sputtering gas on the growth of nano structure. All the substrates were investigated by atomic force microscopy (AFM).

Growth of Carbon Nanotubes and Carbon Nanowalls: Thermal chemical vapour deposition technique was applied to grow carbon materials ranging from carbon nanowalls to carbon nanotubes. Substrates were placed in the ceramic boat and push into the centre of furnace. Argon (Ar) gas with a flow rate of 200 sccm was fed into the quartz CVD reactor in order to prevent the oxidation of catalytic metal while raising the temperature at 350°C. Then H_2 instead of Ar was introduced until 500°C as a dilution gas. The purities of the gas employed in the experiment are all higher than 99.5%. Mixture of acetylene, ammonia and hydrogen with 20:80:100 (sccm) flow ratio were fed into a quartz tubing chamber, respectively in atmospheric pressure. Reaction time and temperature for the growth was 30 minute in 600 °C. The reactor was cooled down slowly to the room temperature (25°C) under Ar atmosphere. The samples were analyzed by a scanning electron microscope (SEM) (XL30, 15-30.KV, Philips Company) in order to measure the alignment, density and type of carbon nanostructures. Structure of the samples was investigated by Raman Spectroscopy (Thermo Nicolet).

RESULT AND DISCUSSIONS

Effect of Sputtering Gas: Fig.1 shows the AFM images of single layer and multi layers thin films glass/Iron, glass/Aluminium, glass/ Iron/ Aluminium deposited on the glass (substrate) with Nitrogen and Argon by DC magnetron sputtering technique. The entire characteristic was mentioned in Table1. Average roughness of sample in same condition increased when Argon was used as a sputtering gas.

The process of CNTs and CNWs /TCVD formation depends on variety of experimental conditions like temperature, basic pressure, reaction time, hydrocarbonic and dilution gases and flow rate of the gas and catalyst. We need to optimize these parameters for such a complex process. Because of the complexity of this problem and our aim to recognize and control the most crucial experimental conditions in the CVD deposition process, we have focused on the effect of catalyst and sputtering gas on the substrate. For these parameters we figure out the growth condition at a fixed optimum condition. Figs 2(a-h) show the typical SEM images of CNTs and CNWs film fabricated by TCVD employing $C_2H_2/NH_3/H_2$ (20:80:100 sccm) mixture for 30 min at atmospheric pressure and a substrate and system temperature of 600°C. These images (a, b) show growth of CNTs on glass\ Al sputtered by nitrogen. The majority of long CNTs were grown on whole substrate are helical and have worthwhile long length.

Table 1: Average roughness for each sample and characterization of 2D AFM image

sample	Region	Rp-v	Rms rough	Ave rough	Mean Ht
Glass\Fe (N2)	[A]	14.1 Å	1.45Å	1.02 Å	6.78Å
Glass\Fe (Ar)	[A]	42.3 Å	4.53 Å	3.50 Å	19 Å
Glass \Al (N2)	[A]	45.8 Å	5.26 Å	4.06 Å	28 Å
Glass \Al (Ar)	[A]	57.9 Å	5.07 Å	4.29 Å	26 Å
Glass\Fe\Al (Ar)	[A]	73.2 Å	9.49 Å	7.38 Å	33.5 Å

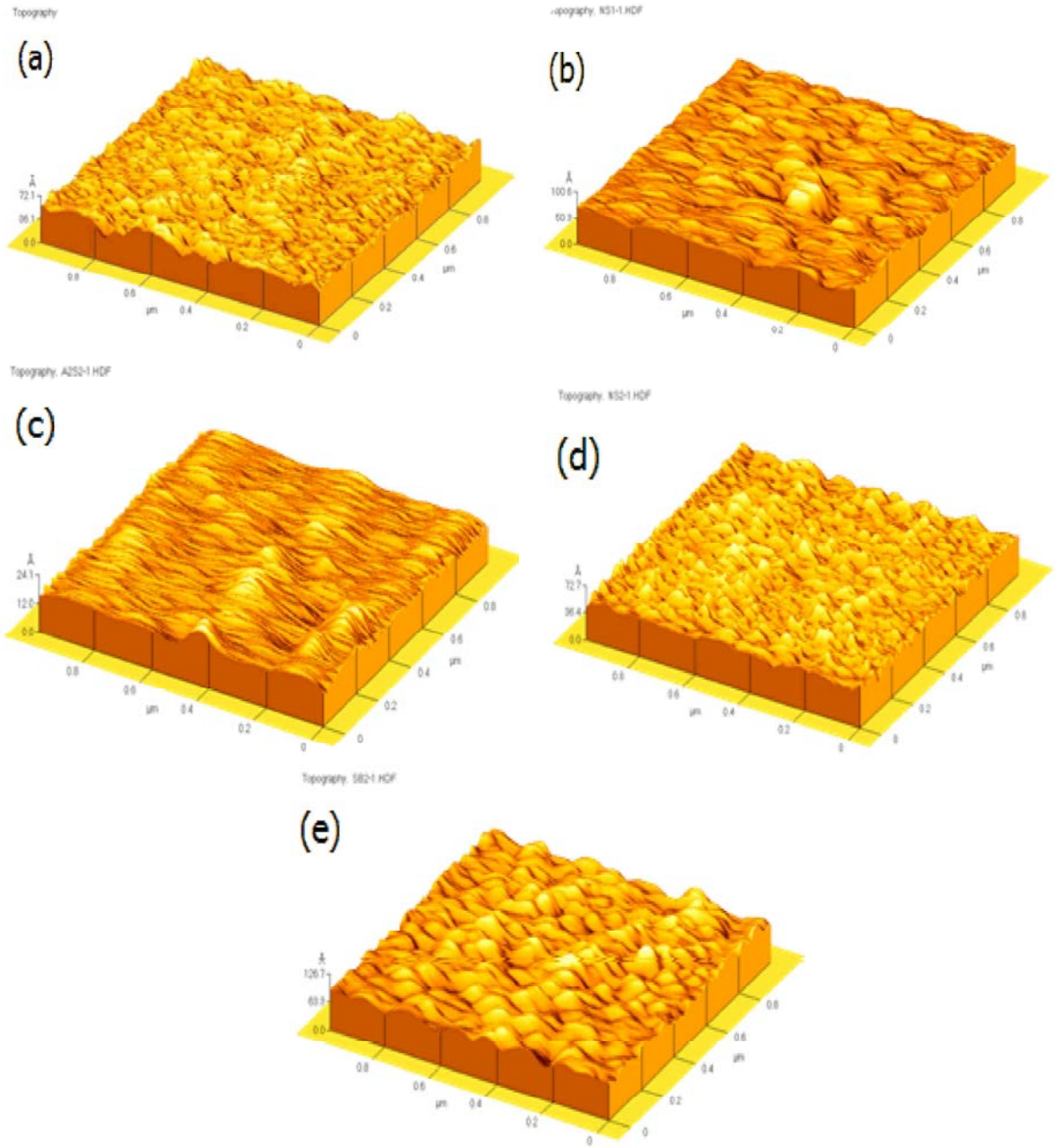

Fig. 1a-e: AFM image of coating surface a) Aluminium coated on glass substrate by Nitrogen as sputtering gas, b) Aluminium coated on glass substrate by Argon as sputtering gas c) Iron coated on glass substrate by Nitrogen as sputtering gas d) Iron coated on glass substrate by Argon as sputtering gas e) Iron and Aluminium coated

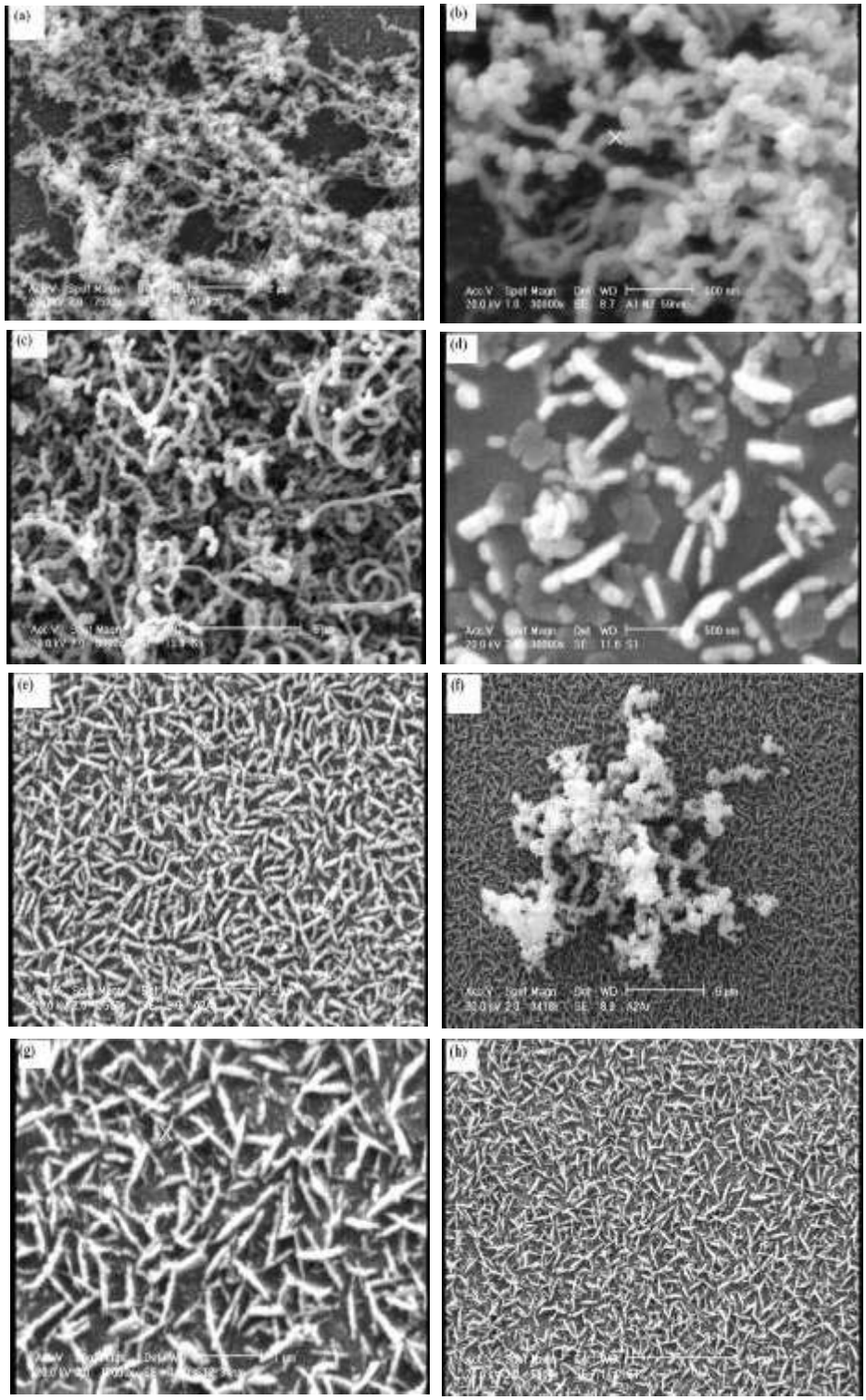

Fig. 2a-h: The SEM image of CNTs and CNWs grown on metallic substrate under atmospheric pressure and low temperature by CVD. (a, b) CNTs on the substrate of Glass\ Al, using nitrogen as sputtering gas. (c) CNTs on the substrate of Glass\ Fe, using nitrogen as sputtering gas. (d) CNWs on the substrate of Glass\ Al, using argon as sputtering gas. (e, f) CNWs on the substrate of Glass\ Fe, using argon as sputtering gas. (g, h) CNWs on the substrate of Glass\ Fe\ Al, using argon as sputtering gas

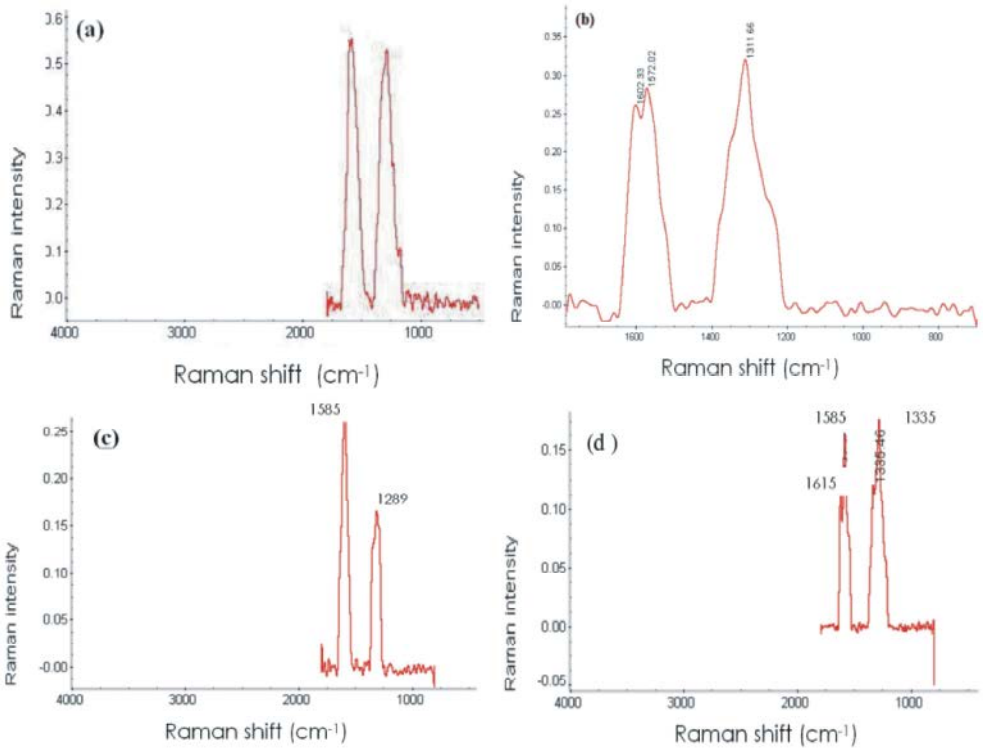

Fig. 3a,d: Typical Raman spectrum of CNTs and CNWs. (a) CNTs synthesized on glass\ Al with nitrogen as sputtering gas . (b) CNWs synthesized on glass\ AL with Argon (C) CNTs synthesized on glass\ Fe with nitrogen as sputtering gas (d) CNWs synthesized on glass\ Fe with argon as sputtering gas

Additionally, there are some carbon particles or bean-sprouts-shaped carbon materials on the surface. Measured thickness of CNTs on image (b) is 59 nm. In figure 2(d, e), by changing sputter gas to argon in same technique by dc magnetron sputtering and same condition in TCVD, carbon nanowalls were grown. It is composed of two-dimentional carbon nanosheets standing vertically on the substrate; the thickness of the carbon nanowalls was about 59 nm. The distribution of the nanowalls is uniform over the whole substrate surface. The CNWs have flower and leaf shape. Al thin film is better catalyst layer for synthesize of CNTs in compare to Fe. Figure 2. (b, c). For proving the effect of sputtering gas and synthesize of carbon nanowalls, we sputtered Fe with Argon on glass with same technique and condition; Fig 2(d,e). Surprisingly, CNWs were grown on whole surface of glass\ Fe substrate with blade shape. The thickness of CNWs is 75 nm. The thickness of CNWs were decreased by synthesize on multilayer thin films (glass\Fe\Al) that sputtered with Argon. We use Raman spectroscopy to investigate, the structure of CNTs and CNWs.

Figure 3. Shows the Raman spectra of the CNTs that synthesized with C_2H_2 /NH_3/H_2 as a hydrocarbonic and dilution gases. Two sharp peaks at around 1330 cm $^{-1}$ and 1580 cm^{-1} reveal the CNTs were grown on substrate. The strong signal at about 1580 cm^{-1} is attributed to the G-band of tangential mode of the graphitic structure and characteristic of a SP^2- hybridized carbon material, while the peak around 1330 cm^{-1} is the D-band corresponding to the defects or limited dimensions of CNT crystal structure. Generally, the G band indicated highly crystalline graphite layer, but D band indicates the existence of defects in the graphitic layer. Moreover, Raman spectrum for CNWs was found to have G bond peak at 1580cm^{-1} indicating the formation of a graphitized structure and D band peak at 1320cm^{-1} corresponding to the disorder-induced phonon mode. The G and D peaks are comparable in intensities. It is noted that the G band peak is accompanied by a shoulder peak at 1610 cm^{-1} (D band).This shoulder peak is associated with finite-size graphite crystals. The strong D band peak suggest a more nanocrystalline structure and presence at graphene edges and defects such as distortion, vacancies and straining to graphitic lattices which are prevalent features of CNWs.

CONCLUSION

We have studied the effect of sputtering gas, Iron and Aluminium thin films, on the growth and structure of CNTs and CNWs under the low temperature and atmospheric pressure by thermal chemical vapour deposition. By investigate the average diameter, distribution and the density, we find that aluminium thin film which is sputtered by Nitrogen is suitable for synthesize of CNTs in compare to Fe. Additionally, in the same condition by changing sputtering gas in the same substrate, CNWs were grown successfully on Fe and Al thin films. By coating Al on Glass\Fe with Argon as a sputtering gas, the thickness of CNWs decreased.

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