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Research Article

Structure of Carbon Nanotubes Grown by Arc-Discharge Technique under Argon, N_2 and O_2 Atmosphere at Different Conditions

Izzat M.AL-Essa†, Ghazala Y. Hermiz†*and Ghuson H. Mohammed†

†University of Baghdad, College of Science, Department of Physics

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Abstract

Carbon nanotubes powder and thin films were prepared by arc-discharge technique at room temperature on glass substrate and silicon wafer under different pressure (10^{-3}, 10^{-4}, and 10^{-5}) mbar of Ar, N_2 and O_2 gases from graphite rode. Thickness of the film is 350nm .The nanotubes were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), atomic force microscopy (AFM) and energy dispersion X-ray analysis (EDXA).X-ray diffraction studies under different annealing times (10, 20 and 30) minute at fixed temperatures is measured. Also effect of gas pressure on the structural of the films was examined. The XRD analysis showed that CNT powder was nearly amorphous and peaks appear which indexed on the basis of the hexagonal graphite nature of the CNT when treated in acid treatment. The XRD of CNT thin films grown in Ar and N_2 atmosphere show the same results under annealing time, with contrast with O_2 atmosphere.

***Keywords**: Carbon nanotubes-arc discharge-structure.*

Introduction

Since the discovery of carbon nanotubes by Iijima in the early nineties the scientific activities in this field have followed an exponential increase due to the remarkable physical properties of this novel form of carbon. Carbon nanotubes(CNTs) can be visualized as a graphene layer, essentially a sheet of graphite, which has been rolled up to form a tube. They have interesting properties due to their one-dimensional structure and giant molecular nature. They are either metallic or semi-conducting depending on the diameter and chiralityp. CNTs are carbon nanostructures of a small diameter on the nanometer scale with one or more walls, and a length large in comparison to the diameter. They have mechanically and chemically stable carbon shells which can be opened filled and closed again without losing their stability

Carbon nanotubes can be obtained in soot after arc-dischargeor laser ablation of graphite rod. The CNTs prepared by these procedures contain impurities like fullerenes, metal catalyst particles that are most often coated with layers of carbon, generally in the amorphous form. The samples have been purified by various methods. Hydrothermal treatment has been used by Tohji*et al*to remove the amorphous carbon from the nanotube surface. Smalley and coworkers have used micro-filtration to eliminate the amorphous carbon and catalyst particles. Martinez *et al* have used microwave acid digestion to reduce the time taken for the purification. High temperature annealing of the purified samples has been adopted by some procedures.

In order to clarify the effect of pressure gases, CNTs were grown in argon, oxygen and nitrogen atmosphere under different pressures (10^{-3}, 10^{-4}, and 10^{-5}) mbar. In this paper a simple procedure to purify CNT produced by the arc discharge method was used. The powder was purified by acid treatment HNO_3 while high annealing temperatures under high vacuum was used in purification of thin films.

Experimental

Arc discharge evaporation method in a high vacuum and low pressure was used to evaporate carbon nanotube thin films; this method is a direct film deposition technique in which the material is deposited by vaporization after plasma is produced. DC current of approximately 50 ampere with voltage of 25 volt was applied between two graphite rods with purity 99.999% and diameters of 3cm and 7cm as an anode and cathode electrodes, respectively. Carbon nanotubs (CNT) thin films were synthesized on Si substrates in argon, nitrogen and oxygen gas as the atmosphere under the various pressure (10^{-3},10^{-4},10^{-5}) mbar. After the arc was carried out, much soot was deposited on the chamber wall. When the powder was

*Corresponding author: **Ghazala.Y.Hermiz**

collected from the chamber, it contained much amorphous carbon and this is purified as follows:

Firstly the soot was placed in a beaker containing of 5ml concentration of HNO_3 and 10ml distilled water stirred in at 323 K for 1/2 h in order to dissolve the amorphous carbon. The sample was washed with distilled water, dried and dispersed in ethanol under sonication and filtered using filter paper. To insulate the amorphous carbon from carbon nanotube powder the sample were collected on the filter paper and dropped onto a copper grid for microscopy observation on a transmission electron microscopy (TEM) operating at voltage 60KV.

Purification for carbon nanotube thin films is annealing at fixed temperature about 773K and various annealing time (10, 20, and 30) min under high vacuum pressure about 10^{-6} mbar using coating unit type Blazer Union BAE 370. The thickness of carbon nanotube thin film 350nm.was measured by using an optical interferometer method employing He-Ne laser (0.632µm) with incident angle 45°.

The nanotubes were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), atomic force microscopy (AFM) and energy dispersion X-ray analysis (EDXA).

The particle size (D) of these materials was calculated from Scherre relation:

$$D = \frac{K'\lambda}{\beta' \cos\theta} \quad (1)$$

Where D is the crystallite size, λ is the x-ray wavelength used which is equal to 1.54A°,β' is the angular line width at half maximum of intensity, θ is the Bragg's diffraction angle and K' is a constant with a value of 0.9.

Result and Discussion

Figure 1 shows a typical EDXA spectrum for CNT deposited on Si substrate.The extreme positions are consulted using the energy tables for characteristic x-ray transitions to establish the elements present. EDXA proves that the obtained heterostructures are composed of carbon, silicon, and oxygen and EDX is selectively contrasted with the characteristic x-ray radiation emitted by carbon (C), oxygen (O), and Si respectively. It is clear from this figure that the fine lines of energy of carbon appear at 0.285 eV. Such energy value is similar to that reported for CNT by Roy *et al.*They found that the binding energy for CNTs prepared by arc discharge lies at 0.285 keV. It can be noticed from the figure that Si peak is detected clearly in the spectrum which belong to substrate material (Si wafer). Another peak of significant intensity is from oxygen atoms appear in the spectrum at of 0.55 keV due to the film growth in oxygen atmosphere. A metallic gold standard electrode is used; hence Au peak is observed in the EDXA spectrum

TEM image of the as-synthesized CNTs as a powder grown by arc-discharge technique at various pressure of Ar, N_2, O_2 atmosphere and purified CNTs, respectively see figure 2 a ,b ,c &d .A greatest soot is exist in the samples beside of that it contains amorphous carbon, particles, where this is an indication that no tubes are observed in this image but a number of nanotubes were covered by the soot and this is characteristic of arc-discharge technique as referred by Huang. Another feature was observed, that the surface is smooth in the high pressure range, whereas it tends to be rough in the low pressures. This consolidates the idea that it is necessary to work in the high gas pressure of the deposition film. Also, it is observed that at high gas pressure of deposition, the quantity of CNT is increased. It observed from figure 2d that the tubes grown in Ar atmosphere are present clearly after purification in HNO_3.

The morphological characteristics of CNT thin films have been studied using Atomic Force Microscope (AFM) to observe nanostructure. Figure 3 shows the surface topographical images recorded for CNT thin films grown by arc discharge technique on glass substrate in Ar, N_2 and O_2 atmosphere. AFM images of the films reveal a structure with dense grains, crystalline structure and clear grain boundaries which became apparent at Ar gas.

Figure 4 a,b and c shows the powder XRD pattern of CNT as-synthesized and purified prepared at Ar , N_2 and O_2 gases, respectively. The powder was collected from the chamber of evacuated system. It is well known that during the synthesis of carbon nanotubes several impurities appear including soot, amorphous carbon and non-tubular graphitic entities. Therefore, a subsequent purification treatment is sometimes required. In our purification procedure, acid treatment is used to produce less impurity. The obtained soot was purified by acid treatment in HNO_3 solution with a stirrer at 323 K for half hours. It is clear from these figures that the peaks related to the interplane, corresponding to indices of graphite (100) at $2\theta = 16.2^0$ are found in all as- synthesized powder of MWCNTs before purification. Other peaks (002) and (004) diffraction lines which correspond to $2\theta=26.2^0$ and $2\theta=56^0$ are not observed in the case of as-synthesized MWNTs and appears as a large peaks in the case of acid-treated MWNTs and the peaks are indexed on the basis of the hexagonal graphite nature of the CNT. This can be due to the amorphous carbon covering the synthesized MWNTs, as observed in the TEM images. This result is in agreement with Vivekchand and Govindarji. They found that the non-purified SWCNTs were amorphous, and after purification, the (10) peak is observed.

The purified powder under Ar, O_2 and N_2 at pressure 10^{-3} mbar shows maximum intensity and a sharp peak at (002) direction which indicates that the sample is pure and nearly does not contain any amorphous carbon.

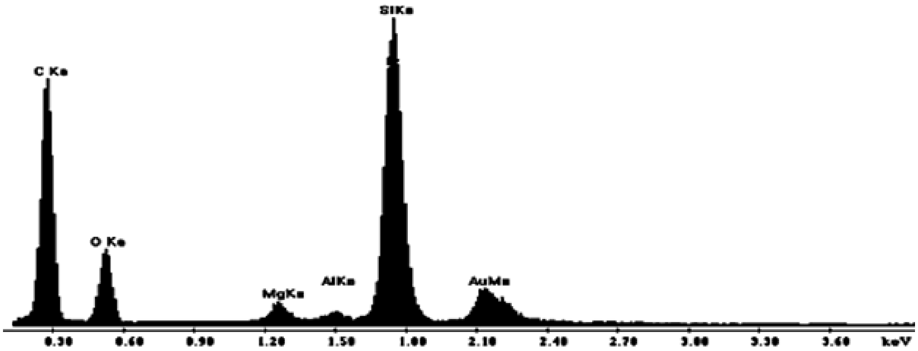

Figure 1 EDXA spectra for CNT thin film grown in oxygen atmosphere on Si substrate

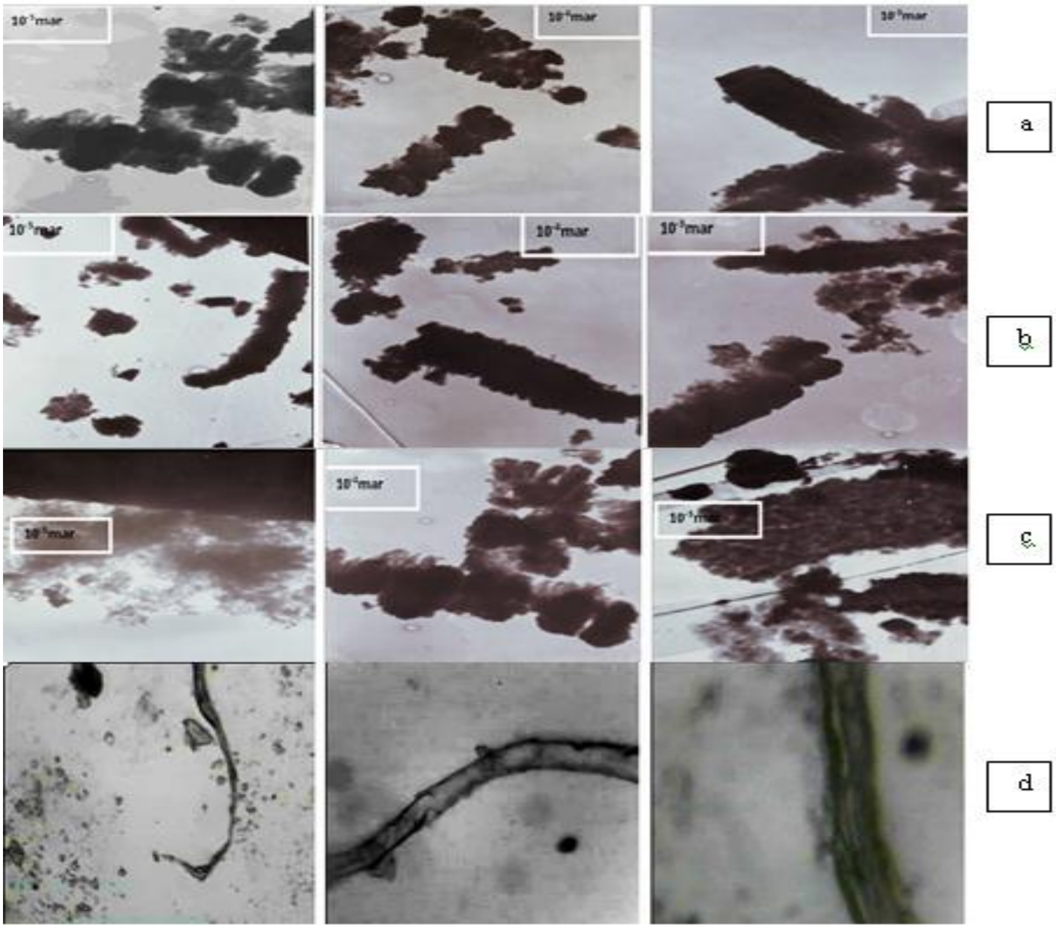

Figure 2 TEM images of CNTs grown in a-Argon atmosphere with magnification X3400. b-Nitrogen atmosphere with magnification X12000 c-Oxygen atmosphere with magnification X16000d-Purified CNTs by HNO_3acid with magnification X92000

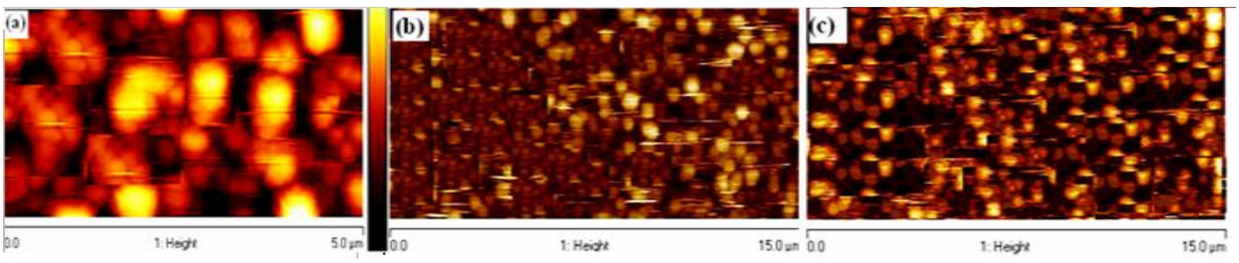

Figure 3 AFM image for deposited CNT thin films grown under pressure 10^{-3}mbar of different gases a-Ar gas, b-N_2 gas and c-O_2 gas

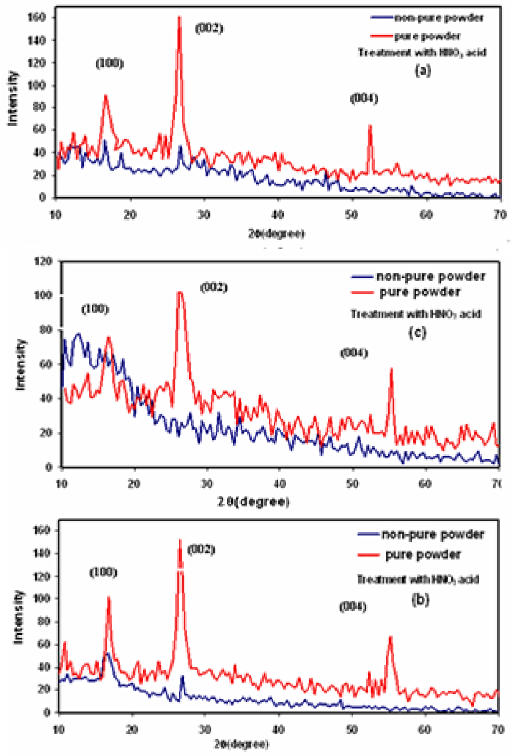

Figure 4 X-Ray diffraction patterns of MWCNT's as powder for as-synthesized and purified by acid-treated samples prepared at a-Argon, b-Nitrogen, c-Oxygen gas pressure 10^{-3}

Figure 5 a and b shows the dependence of the XRD patterns on the annealing temperature at different times (10,20,30) min and fixed temperatures 773 K for CNT thin films grown under pressure 10^{-3} mbar of Ar and N_2 gases, respectively. The XRD spectra of the CNT thin films grown in Ar and N_2 atmosphere show the same results, indicating that the crystallinity of the films depends on the annealing temperature rather than atmosphere. No significant sign of structural transformation was observed in the X-ray diffraction patterns until annealing temperature 30 min.

The annealing treatment has affected both the full at half maximum (FWHM) intensity, and the peak position of XRD patterns obtained from the CNT thin films by which the peak height decreases while the peak width increases with increasing the annealing time. The FWHM values are related to the particle size of the film. The smaller the FWHM, the larger the particle size and the better the crystal quality of the whole film. By increasing the annealing time, the particle size of film was decreased (increase the values FWHM for the film grown in the Ar and N_2 atmosphere) as shown in Figure 5a and b and Table 1. The peak related to the interlayer length, corresponding to indices of graphite (100) reflection shows a remarkable annealing times-dependence by which the value of d_{100} andthe intensity of the peak decreases with increasing annealing time and shifts toward the higher 2ϴ value .

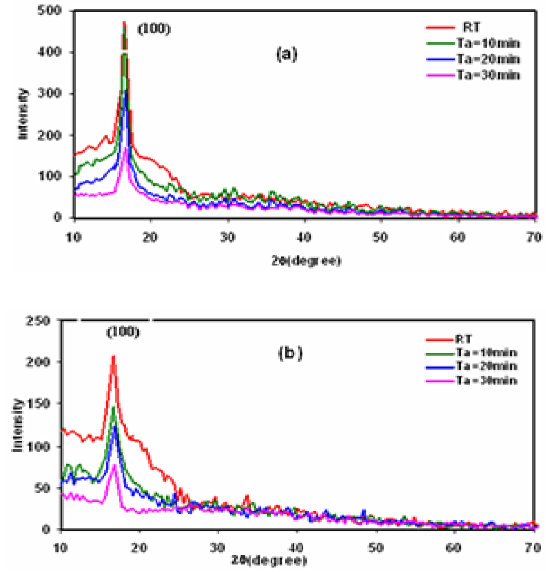

Figure 5 X-ray diffraction patterns of CNT thin films grown in a-argon and b-nitrogen atmosphere under different annealing times

Figure 6a-d shows the x-ray diffraction pattern for CNT thin films grown in O_2 atmosphere and the effect of heat treatment is present. In all prepared films, XRD analyses show that the carbon tubes are hexagonal polycrystalline with a strong (002) orientation. Also, it is observed that the peak position significantly shifts to the higher angleside on heating. Such behaviors are well understood by desorption of the materials, such as O_2, N_2, and other impurities, from the bundles with increasing annealing times .Our results is contrasted with the result emphasized by Yutaka Maniwa[17] for MWCNT obtained from arc-discharge. Their results show that the peak intensity strongly temperature dependence and shifts toward lower angle with increasing annealing temperature i.e. interlayer distance d increases with increasing the annealing temperature and another paper for Yutaka Maniwa show that (10) shifted to lower angle with increasing annealing temperature for SWCNTs grown in hydrogen atmosphere, while Hitoshi and Tetsufound found that the peak corresponding to indices of graphite (002) and (004), exhibited large shifts toward higher angles with increasing pressure. Also, it is noticed a strong asymmetry, "sawtooth" shape, for peaks. This is a characteristic of turbostratic graphite lacking interlayer stacking correlation. The increase of the intensity for the (002) peak in the case of O_2 gas with increasing of annealing times means the improvement of the crystal structure in that direction as shown in figure(6a,b,c and d) and Table (2). Also, from the same Table it is observed that the interlayer spacing decreases with increasing annealing times and the value of ($d_{(002)}$ = 3.372A ˚) for a deposited film is similar to that of graphite $d_{(002)}$ = 3.35A.This is attributed to the recrystallization in the MWCNTs thin films which takes place through annealing the films.

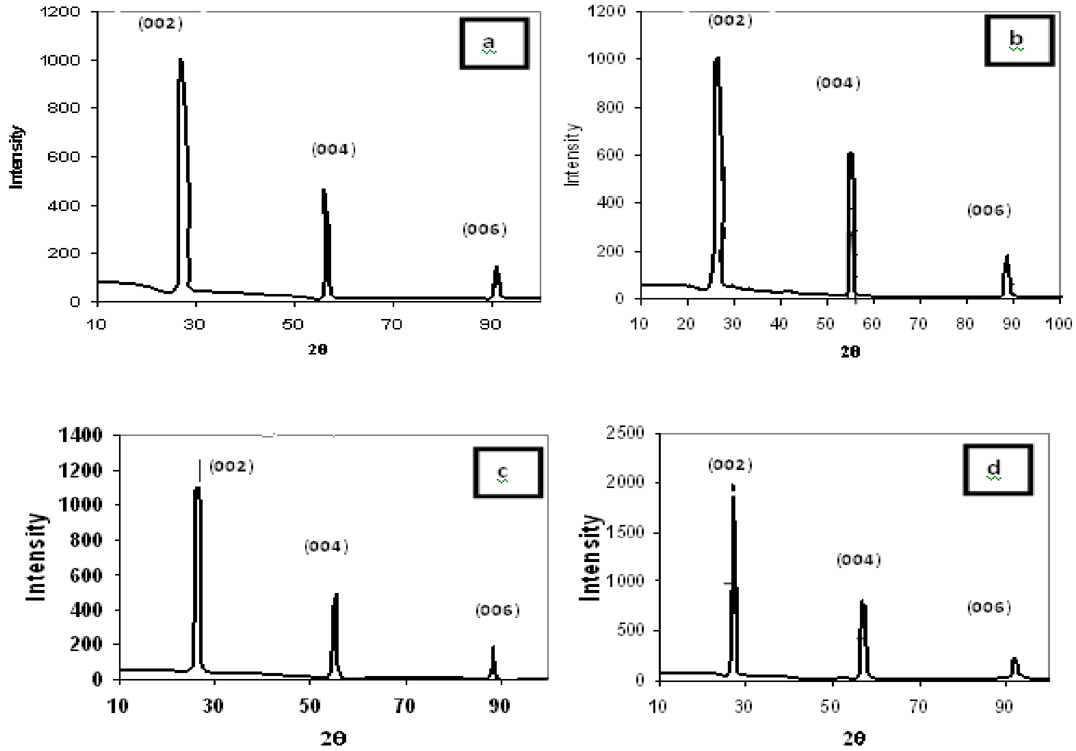

Figure 6X-ray diffraction patterns of CNT thin films grown in Oxygen atmosphere under different annealing times: a-as –deposit film, b-10min,c-20min,d-30min

Table 1 Values of 2θ,d and D for CNT thin films for argon ,nitrogen gases under different annealing times

Pressure(mbar)	Gas	Annealing Time(min.)	hkl	2θ(degree)	$d_{exp.}$(A°)	D(nm)
10^{-3}	Argon	as-deposit	100	16.50	5.366	6.690
		10	100	16.60	5.330	5.947
		20	100	16.65	5.130	4.723
		30	100	16.70	5.302	4.460
10^{-4}		as-deposit	100	16.67	5.311	4.400
10^{-5}		as-deposit	100	16.72	5.290	3.570
10^{-3}	nitrogen	as-deposit	100	16.6	5.330	4.460
		10	100	16.7	5.302	4.220
		20	100	16.75	5.286	3.490
		30	100	16.82	5.264	3.410

Table 2 Values of 2Θ, d and D for CNT thin films for O_2 gas under different annealing times and gas pressure 10^{3}mbar

Gas	Annealing Time(min.)	hkl	2θ(degree)	$d_{exp.}$(A°)	D(nm)
Oxygen	as-deposit	002	26.4	3.372	4.080
		004	54.99	1.667	5.970
		006	88.44	1.104	4.430
	10	002	26.9	3.31	5.440
		004	55.6	1.65	5.440
		006	88.6	1.102	4.350
	20	002	27	3.298	6.050
		004	55.8	1.65	5.140
		006	90	1.088	7.490
	30	002	27.06	3.291	7.296

We conclude from these results that the full width at half maximum (FWHM) of the (100) peaks is changed by increasing with increasing annealing times for Ar and N_2 gas while for O_2 gas the (FWHM) for (002) peak decreases with increasing annealing time.

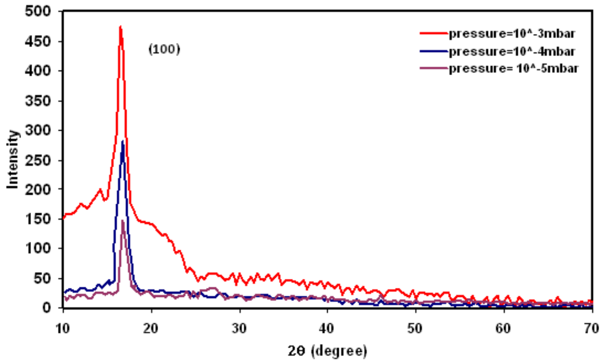

Figure 7 X-ray diffraction patterns of CNT thin films at different pressure of Argon atmosphere

The effect of gas pressure on the structure of CNT thin films at room temperature was studied. It is found from figure 7 that no significant sign of structural transformation was observed in the X-ray diffraction patterns until 10^{-5} mbar and the graphite (100) exhibits large shifts toward higher angles with decreasing gas pressure. The intensity of these peaks also changed during the increase of the pressure. This behavior can be explained by the film growth at low deposition pressure is slower than that at high pressure. At lower gas pressure and due to the thin plasma density, the ion bombardment of growing film leads to increase the compressive stresses in the deposited films, making the films compact and denser with the increasing deposition gas pressure and then highly energetic ion bombardment changes.

The full width at half maximum of the (100) peaks were changed at all pressures. This result obviously contradicts with Hitoshi Yusa and TetsuWatanuki. They suggested that the full width at half maximum (FWHM) of (002) peaks keeps a constant.

By using the Scherrer's formula 1, the crystallite size (D) of the CNT films have been calculated and given in Tables 1 and 2. It is evident from the Tables that the grain size of CNT thin films increases slightly with increasing the gas pressure but decreases with increasing the time of annealing for films grown in Ar and N_2 atmosphere. While for films growth in O_2 atmosphere, it is noticed that the grain size increases with increasing annealing times which can be deduced from the lower full width at half maximum (FWHM) of diffraction peaks.

Conclusion

a. The arc-discharge technique was identified to offer a more promising route to develop scalable carbon nanotube production technique under various pressure of Ar, N_2 and O_2 gas.
b.The XRD analysis showed that CNT powder was nearly amorphous and peaks appear which indexed on the basis of the hexagonal graphite nature of the CNT when treated in acid treatment. The XRD of CNT thin films grown in Ar and N_2 atmosphere show the same results under annealing time, with contrast with O_2 atmosphere.
c. The pressure dependence of XRD pattern for CNT thin films shows the preferred orientation (100) which exhibits large shifts toward higher angles with increasing gas pressure i.e improved in crystalline in the case of Ar gas.

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