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CNTs' array growth using the floating catalyst-CVD method over different substrates and varying hydrogen supply

O. Guellati[a,b,c,*], D. Bégin[b], F. Antoni[e], S. Moldovan[d], M. Guerioune[a], C. Pham-Huu[b], I. Janowska[b,*]

[a] Laboratoire d'Etude et de Recherche des Etats Condensés (LEREC), Département de Physique, Université Badji-Mokhtar de Annaba, BP. 12, Annaba 23000, Algeria
[b] Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES) – ECPM – CNRS – UMR 7515 Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France
[c] Université de Souk-Ahras, BP. 1553, Souk-Ahras, 41000, Algeria
[d] Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 du CNRS, Université de Strasbourg, France
[e] Laboratoire ICube – DESSP (UMR7357 CNRS, Université de Strasbourg), 23 Rue du Loess – BP20, 67037 Strasbourg Cedex 02, France

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ABSTRACT

In the present investigation, we point out the effect of the substrate crystallinity on the growth rate, efficiency, quality and the structure of synthesized aligned carbon nanotubes (CNTs). Three substrates are tested: amorphous alumina (Al_2O_3), silica (Si/SiO_2), and crystalline alumina (sapphire). The growth is carried out using the floating catalyst-CVD process with the ferrocene-toluene solution as precursor. In addition, different concentrations of H_2 in the gas supply are investigated. It is observed that the sapphire substrate provides a more homogenous forest of vertically oriented straight nanotubes with small diameter, despite initial horizontal alignment of the nanotubes. In the presence of H_2, long arrays of high L/Φ aspect ratio nanotubes were obtained with a reduction of diameter and the number of walls. L/Φ aspect ratio in the case of 7% H_2 is c.a. 3600 for sapphire substrate, 1500 and 2000 for alumina and silica amorphous substrate, respectively. When sapphire substrate is used, the increase of H_2 to 15% provides the L/Φ aspect ratio of ~14,000.

1. Introduction

The efficient exploitation of CNT properties, such as mechanical, electrical or surface area is often requiring alignment of the tubes. The alignment of high density CNTs to a required direction are under investigation for a wide range of practical nanotechnology applications, such as high performance electronic and optoelectronic nano-devices such as CNT based field-emission devices, transistors, diodes and resistors, electrochemical energy storage devices like CNT supercapacitors, gas sensors, heterogeneous catalysis, hydrogen storage, … [1–3]. More research efforts are required however to control not only their direction but also the structural quality of the arrays and nanotubes themselves as advanced solid-state materials.

Two classes of alignment techniques can be distinguished from growing the tubes along a given direction, either horizontal or vertical depending on the substrate crystallinity [4–7]. To control them, it is important to understand their nucleation and their growth processes. The CNT-CNT or the CNT-substrate interactions, in addition to the arrangement and activity of the catalytic sites, determine the CNTs grow in an isolated, tangled or aligned configuration [8–10]. Moreover, the strong influence of atomic arrangement of surface such as sapphire is suggested not only to influence the growth direction but also the tubes chirality [11,12]. In the case of catalyst deposited on the substrate before the growth of CNTs is initiated, the alignment is only horizontal to the substrate. In turn, generally, at higher catalyst density and CNT growth rate, a vertically aligned "VA" growth mode is favourable; the CNTs self-orient perpendicularly to the substrate due to an initial crowding and continue to grow upward in this direction [10,13].

In contrast to previous synthesis method, floating catalyst CVD is promising for in-situ nucleation and growth as one step efficient method, but also quite versatile for scale-up production of selective CNTs [14]. Depending on different processes and growth system designs, the growth rates of CNTs using this method can be limited by basic parameters such as substrate features, substrate-catalyst contact energy, catalyst poisoning and hydrocarbon precursors, … [4,15,16]. There are a number of reports on production of CNTs based on continuous CVD route discussing either the experimental [14–24] or theoretical [25–30] factors of the process. Besides these, the kinetic aspects

* Corresponding authors at: Laboratoire d'Etude et de Recherche des Etats Condensés (LEREC), Département de Physique, Université Badji-Mokhtar de Annaba, BP. 12, Annaba 23000, Algeria (O. Guellati).
E-mail addresses: ouanassa.guellati@univ-annaba.org (O. Guellati), janowskai@unistra.fr (I. Janowska).

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such as local reaction rates at the catalyst surface, diffusion of precursor to the catalyst through as grown CNTs and catalytic surface poisoning by other formed carbonaceous species are actually the subject of important studies [17,31]. Mainly, the role of H_2 has been described quite extensively in both the vapour grown carbon fibres and the carbon nanotubes literature. H_2 is known to have the ability to either accelerate or suppress the formation of carbon [26,27]. It has also been shown for this type of process that H_2 can also plays an important role in the control of the CNTs diameter as reported in our previous work by studying the synergetic effect of EtOH/hydrogen on the growth rate of VA-MWNTs [17], brakes the deposited catalyst layer into smaller particles [16] as well as helps to prevent the formation of amorphous carbon impurities [18,19]. The H_2 concentration should be however low enough to avoid excessive surface carbon removal by the formation of CH_4, which would lead to a formation of lower CNT yield [31].

The organisation of CNTs into horizontally and vertically aligned arrays on surfaces, which continues to be a major challenge in controlled production of macroscopically CNTs, has been significantly advanced by the development of directional flow or substrate domain [16,18]. More recently [19–21], aligned growth by epitaxial orientation on well defined crystal surfaces, directed by atomic steps, nanofaces or atomic rows or by applied electrical field, has opened up new ways of organizing CNTs on surfaces into perfectly aligned arrays.

Ago's group have proposed, lately, a new method based on atomic arrangement as guide and specific crystallographic growth direction [5,6,8,11,19]. They tried to understand the role of catalyst-surface interactions onto different substrates such as sapphire, basing, on their surface energy that affects the surface diffusion length, the catalyst particle size and the CNTs density. In addition, the difference between base or tip growth mechanism is often explained in terms of adhesion force strong or weak adhesion, respectively between the catalyst particle and the substrate. An important effect of Al_2O_3 substrate was found on the production of highly dense and nanosized Co particles, owing to a low surface diffusivity, and reduced agglomeration of metal atoms [10].

In this investigation, we show a study on the influence of the substrate crystallinity on the growth and the morphology of macroscopic CNTs obtained with floating-catalyst CVD process, assisted or not by H_2. In this regard, the CVD process with ferrocene dissolved in toluene ($FeCp_2$-toluene) as floated catalyst has been conducted on crystallinized sapphire wafers and amorphous alumina. Additionally, the Si/SiO_2 wafers were tested in the same conditions. The effect of H_2 concentration (0, 7 and 15 vol%) in Ar flow on the MWNTs alignment selectivity, density and crystallinity of the formed arrays and nanotubes themselves have been investigated as well.

2. Experimental section

2.1. Synthesis of aligned carbon nanotubes "VACNTs"

All samples were prepared by a floated-catalyst CVD (Fig. 1) by injection of a constant concentration of the ferrocene "$FeCp_2$"-toluene (20 g/L) with a constant flow rate of carrier gas (Argon "Ar", 1.5 L/min) and with hydrogen "H_2" gas addition (7 and 15 vol% of Ar or 0 vol%). So, the total gas supply will be 1.5 L/min Ar + 0.105 L/min H_2 = 1.6 L/min.

In these conditions, a total amount of 20 mL of the $FeCp_2$-toluene solution is injected continuously with the flow rate of 0.33 mL/min into the heated reactor using a programmable syringe system.

The substrates used for the oriented growth of the arrays using floated CCVD are: silicon wafers (Siltronix, Si_{100}, 10 × 10 mm^2 with 525 μm thickness) thermally oxidized to obtain SiO_2 barrier layer of 100 nm thickness, alumina wafers (Crystal, 20 × 10 mm^2 with 0.45 mm thickness) and r-plane sapphire wafers (Crystal, one side polished, [1–102] 15 × 15 mm^2 with 0.45 mm thickness).

In general, the process starts by the evacuation of the air from quartz reactor using Ar flow for 30 min followed by heating the reactor to 870 °C. The temperature is maintained for one hour at atmospheric pressure. Then the solution of Fe-Cp_2-toluene/Ar (and H_2) is injected for CNT array growth. After the synthesis, the reactor is cooled down under Ar flow. According to eye- observations and FESEM analysis, the CNTs growth are carpet (« sheet ») geometry (see Fig. 1b).

After that, the CNT arrays are purified in order to remove the remaining iron catalyst from the samples by acid treatment step using aqua regia (HCl: HNO_3 = 1:3) at 80 °C under stirring during 2 h, then, washed and dried at 80 °C for all the night. The volume density of products was then calculated by dividing the deposit mass by the substrate volume.

2.2. Characterization techniques

JEOL 6700-FEG microscope field emission scanning electron microscope (FESEM) accompanied with Energy Dispersive X-ray spectroscopy (EDX) quantitative analysis was employed to examine the morphology and the purity of products: the length, the orientation and the density estimation were obtained from cross-sectional images of the samples.

JEOL 2100F high and low magnification transmission electron microscopy (TEM) working under an accelerated voltage of 200 kV was carried out with a point-to-point resolution of 0.23 nm in order to characterize the grown CNT microstructure. A drop of dispersed CNTs in ethanol medium was deposited onto a holey carbon coated copper TEM grid for examination.

Tristar Micromeritics sorptometer using nitrogen as adsorbant at liquid nitrogen temperature was used to specific surface area measurements. Before measurements, the sample was outgassed at 250 °C for 3 h minimum in order to desorb impurities and moisture.

Setaram apparatus Thermo-Gravimetry Analysis (TGA) was carried out under air flow (20 mL/min) where the experiments were performed from ambient to 1000 °C with a heating rate of 10 °C/min.

Microraman RENISHAW spectrometer (RAMASCOPE 2000 coupled to an optical microscope with a spot size of 1 μm^2 and 1 cm^{-1} resolution) operated with a He-Ne Laser beam excitation of 632.8 nm wavelength was employed to perform Raman spectroscopy. The D/G peak areas ratio was used for the determination of the defective (~1350 cm^{-1}) to graphitic (~1589 cm^{-1}) carbon ratio present inside the as-synthesized CNT arrays.

3. Results

It is already well established in the literature that the CNT grown on the sapphire substrates are horizontally aligned in the case of the predeposited catalyst due to their interaction with atomically arranged substrate surface [17]. Indeed, in the present investigation, i.e. when floated catalyst is provided in continuous way, the horizontal arrangement is observed on sapphire substrate for the first growth period, while next it changes gradually to vertical orientation. In contrast, the growth on amorphous substrates i.e. silica and alumina wafers (same for quartz reactor walls), the MWNTs are oriented perpendicular to substrate from the beginning as generally observed by researcher using amorphous substrate with same CVD approach [32,33].

In Table 1, the weight, thickness and density of obtained CNT arrays are presented as well as the diameter of the tubes, for different supports and percentage of H_2. These results correspond to the crude CNT arrays without purification step. According to the obtained results reported in Table 1, the MWNT volume density depends slightly on the substrate nature and changes in general with the H_2 concentration in the carrier gas during the growth, especially in the case of sapphire substrate.

The addition of hydrogen decreases the deposited carbon weight and the growth rate for a given substrate due to the carbon etching action, except the sapphire with 15% of H_2. In the latter case despite the low volume density and reduced tubes diameter, the height of tubes