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Low temperature growth of carbon nanotubes by microwave plasma stimulated by CO_2 as weak oxidant and guided by shadow masking

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ABSTRACT

Operating at a moderate MW power of 600 W and employing optimized Fe nanoparticles as catalyst, growth optimization of multi-wall CNTs at a relatively low substrate temperature has been performed using tubular microwave plasma enhanced-CVD system. Moderately high energy density plasma facilitates formation of essential precursors for CNT growth. Two intriguing techniques have been integrated in the growth process. Specific shadow masking arrangement by specially designed stainless steel multiple mask assembly protects the growth surface from etching by direct plasma bombardment. CO_2 has been used as an auxiliary gaseous component added to the (CH_4 + H_2) plasma. Instrumental presence of CO_2 as a weak oxidant in the plasma accomplishes the removal of a-C coverage from the Fe catalyst nanoparticles via etching by atomic O and thereby, re-triggers their catalytic reactivity and ensures the persistent growth of CNTs. Altogether, a perpetual growth of multiwall CNTs has been realized through tip-growth process at the lowest substrate temperature (300 °C) reported so far in PECVD.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima [1] significant researches have been conducted in this fascinating arena of materials science and the progress towards commercial applications of many devices e.g., gas sensors, microelectronic transistors, field emitters etc. has been stimulated enormously [2]. Over the years various techniques have been developed for the growth of CNTs, e.g., arc discharge, pyrolysis, laser ablation, thermal chemical vapor deposition, plasma enhanced chemical vapor deposition (PECVD), etc., and a number of different catalysts e.g. Fe, Ni, Co etc. have been used for growing CNTs from CH_4, C_2H_2 precursor gases [3]. High-quality and well-aligned CNTs are necessary for the applications in the field of microelectronics. Successful growth of vertically aligned multiwall carbon nanotubes over large areas, reported by Ren et al. [4], using plasma enhanced chemical vapor deposition (PECVD) technique, initiated significant interest in the use of this approach for the production of carbon nanotubes for many applications including as electron emission sources in display devices. Various PECVD growth techniques e.g., hot filament (HF-PECVD) [4], DC glow discharge (DCGD-PECVD) [5, 6], inductively coupled plasma (ICP-PECVD) [7] and microwave plasma (MW-PECVD) [8] produce vertically aligned CNTs with a high yield. Even the growth of isolated vertical CNT structures has been reported [9, 10] with high yield and reasonable control [11]. Comparatively high density plasma is required for growing good quality CNT structures. Microwave plasma enhanced chemical vapor deposition (MW-PECVD) is very useful in this context; although, specific nature of the gas precursors and energy of the ions in the plasma are also significant for attaining the precise structures and characteristics of the CNT films.

Using plasma-CVD processes, in particular, carbon nanofibers have been reported to be grown at temperatures as low as 120 °C [12, 13]. However, due to the need of a specific energy for occurring the essential reactions, good quality CNTs are grown at temperatures nearly 600 °C [4–6, 14]. Synthesis of CNTs at low temperature with sufficient yield is very much difficult due to the involved problems in low temperature nucleation. Required energetic environment may be attained by configuring specific modifications around the vicinity of the growing network, and using specific gas phase components to mobilize the growth precursors around the growth zone, in addition to proper optimization of the plasma parameters for growing CNT films even at a low substrate temperature.

A high power plasma is reasonable to create favorable atmosphere for the CNT growth. However, at a high power applied to the plasma, highly energetic ions collision affects the growing CNT surface immediately after the deposition starts. As a result the deposition rate

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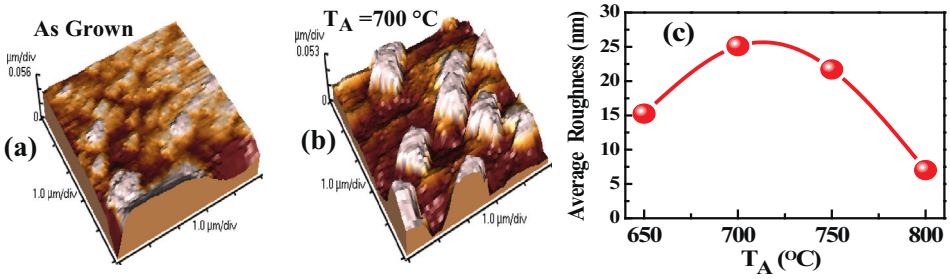

Fig. 1. AFM micrographs of the surface of Fe catalyst layer: (a) as-grown without post deposition annealing, (b) after vacuum annealing at T_A = 700 °C for 1 h. and (c) variation of the average roughness (Ra) of Fe catalyst nano-particle as a function of annealing temperature, T_A.

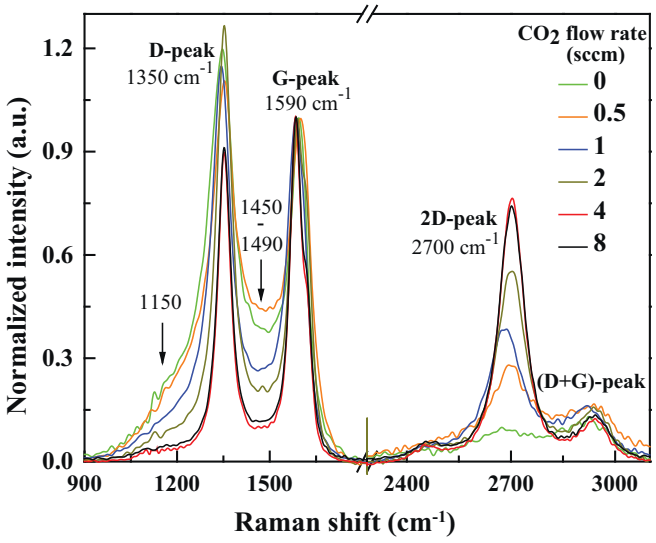

Fig. 2. Raman spectra of CNT films prepared by varying the CO_2 flow rate within the (CH_4 + H_2) microwave plasma.

reduces drastically. To eliminate the deposition rate issue and reduce the surface damage by high energy ion collisions in high power region, a buffering technique may be useful. In this perspective, the diffused plasma may have an important role to play [15]. Actually plasma is an energetic disorder where numerous ion precursors are in energetically random distribution. This energetic radicals or ions disturb the growth process by pulling out the structure which has already formed, although productive molecules are also there which are helpful to form the desired structure. In remote plasma configuration the effect of direct plasma bombardment can be minimized, where ion density reduces considerably and the growth yield decreases inevitably. Required optimization can be realized by introducing specially designed stainless steel mask assembly [15]. Diffused plasma under the mask could have controlled velocity of the impinging ions and the CNT growth zone remains protected from detrimental direct ion bombardment. However, high energy hydrocarbon precursors generated within high density microwave plasma can be simultaneously made useful for providing required activation energy for CNT growth.

Furthermore, CO_2 has been reported to be efficiently used as a weak oxidant in the plasma to selectively etch mostly the amorphous components that oppose the spontaneous growth of CNTs. Thereby, CNTs have been grown at lower temperature, although under a strong negative DC substrate bias [16]. Addition of a metal oxide as a standard catalyst has been reported to yield single wall CNTs (SWCNT) at temperatures lower than that required without the presence of a metal oxide. In presence of metal oxides the SWCNT secondary growth mode has not been a function of some oxygen-modified carbon precursors for SWCNT synthesis. It has been argued that the presence of only a very small quantity of O_2 is needed to prevent MWCNT growth and allow SWCNTs to grow. The growth of SWCNTs is not much induced due to a metal oxide as such, but is induced more due to the metal with oxygen being present [17].

By specific masking of the growth zone and tricky use of oxide precursors as weak oxidant in the hydrocarbon plasma, the present research has been targeted to look into avenues for enabling CNTs to grow at temperatures below the conventional one, in order to make it compatible for directly producing on device structures by reducing effects on other components of the device during fabrication and reducing the production cost, as well.

2. Experimental

An indigenously built tubular microwave plasma enhanced CVD (MW-PECVD: 2.45 GHz, 2 kW) reactor, with 0.45 m long and 80 mm diameter quartz tube as the reaction chamber, was used for the growth of carbon nanotube thin films structures [15, 18]. The reactor was evacuated to a base vacuum ~2×10^{-5} Torr with the help of rotary and turbo pump assembly. During plasma ignition, the flow of the reacting gases was maintained by a booster and rotary combination. CH_4 was used as the source gas and H_2 as the diluent gas; in addition CO_2 was used to play a tricky role as a weak oxidizer. A constant flow rate of CH_4 and H_2 gases was maintained each at 7.5 sccm, using mass flow controllers (Aalborg, USA). CNT films were grown by introducing controlled amount of CO_2 to the (CH_4 + H_2) plasma at 600 W of electrical power applied to the microwave assembly (Sairem, France), 45 Torr of gas pressure measured by baratron gauge (Leybold, Ceravac) and at ~300 °C temperature of the quartz plate used as the substrate. The substrate temperature was measured by a K-type thermocouple integrated on the back surface of the stainless steel substrate holder which was heated through internal heating coils placed outside the plasma. In order to record and maintain an accurate growth temperature on the substrate, the temperature controller backing the substrate holder heater was generally set to a magnitude obtained through prior calibration at the non-plasma equilibrium conditions. Before the initiation of MW plasma for CNT growth the substrates were externally heated and kept at an equilibrium temperature of ~300 °C, in particular, which was maintained identical during plasma ignition as well. The stainless steel grid-like multiple mask assembly was designed specifically to generate diffuse plasma on the substrate [15]. Considering a high carbon diffusion rate among other noble metals, Fe was used as the catalyst material for the CNT growth. Furthermore, Fe has stronger adhesion with the growing CNTs and hence considered to be more efficient in forming high curvature CNTs, like SWCNT because of its smaller diameter [19]. Quartz substrates were pre-coated by 5 nm thick Fe catalyst layer deposited by RF magnetron sputtering in Ar^+ atmosphere operated at 180 W power and 30 mTorr pressure. Before using the Fe coated quartz plates as the active substrates, those were annealed at different temperatures between 650 °C to 800 °C varying in step of 50 °C in a vacuum furnace for preparing the Fe nano-particles for their subsequent utilization as the active catalyst for the growth of CNTs. The Fe nano-particles were confirmed by Atomic Force Microscopy (Veeco