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Short Communication

Carbon Nanotubes Grown by CO_2 Laser-Induced Chemical Vapor Deposition on Quartz

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Carbon nanotubes (CNTs) have been synthesized on quartz with multiple catalyst layer (Fe/Al/Cr) and an acetylene–hydrogen mixture as the precursor gas by laser-assisted chemical vapor deposition (LCVD). A CO_2 laser at 10.6 μm was used to directly irradiate the substrates during the LCVD process. It is demonstrated that the fabrication of CNTs can be achieved with a single irradiation for each CNT using LCVD with no annealing or preprocessing of the substrate. Here, laser fast heating is considered the primary mechanism facilitating the growth of CNT.

Keywords: Nanotubes; Laser-induced chemical vapor deposition; Scanning electron microscopy; multiple catalyst layer

1. INTRODUCTION

Rapid progress in the synthesis of a variety of different nanostructures with fascinating electronic and optical properties irreducible to properties of bulk media symbolizes a fundamental breakthrough in the physics and chemistry of condensed media, which significantly extends our knowledge of the nature of solids and our capabilities to control their properties. Despite different physical nature, nanoobjects share the common property of having extremely small dimensions in one or several directions, which are about 1 or 2 orders of magnitude bigger that of the characteristic interatomic distance. Since the discovery of carbon nanotubes (CNTs) by Iijima, they have attracted a lot of interest due to their remarkable physical and chemical properties. Carbon nanotubes (CNTs) are graphene sheets rolled up into cylinders of approximately one nanometer in diameter. In general, carbon nanotubes exist in one of the two forms: (1) a single-wall carbon nanotube (SWCNT), which consists of a single cylindrical graphite sheet, and (2) a multi-wall carbon nanotube (MWCNT) consisting of multiple nested coaxial single-wall nanotubes with an interlayer spacing of 0.34–

0.36nm[1]. Extensive work carried out worldwide in recent years has revealed the intriguing physical properties of these novel molecular-scale wires [2]. Nanotubes have been shown to be useful for miniaturized electronic, mechanical, electromechanical, chemical, and scanning probe devices and materials for macroscopic composites [3]. variety of methods have been developed for the synthesis of CNTs; for example, arc discharge, laser ablation and catalytic chemical vapour deposition (CCVD) [4]. Pyrolytic LCVD is an alternate form of CVD in which a laser beam is used as a heat source to drive the chemical reactions. Because of the small reaction area and high temperature gradient used in LCVD, the deposition conditions and the resulting materials can be very different from those in large area thermal CVD. The pyrolytic laser-induced chemical vapor deposition (LCVD) technique proposed in this study has the potential to overcome disadvantages associated with conventional CVD techniques. The LCVD technique in general has several prominent advantages including high deposition rates of typically 100–1000 times greater than maximum rates obtained by CVD techniques, which is favorable for scale-up production of carbon nanotubes. Second, minimum substrate and grown nanotube damage is observed due to highly localized heating and excellent spatial resolution and process control. Third, temperatures involved in laser chemical processing are generally higher than conventional and LCVD processes, therefore one would expect lower defect densities and a higher degree of graphitization for LCVD produced carbon nanotubes. Furthermore, this LCVD technique has the capability to make carbon nanotube networks and patterns by selected area deposition and laser direct writing techniques. In pyrolytic LCVD, a laser beam is used to locally create a hot spot on the substrate surface. Chemical vapor deposition occurs at the gas–substrate interface when the reactant molecules receive sufficient energy and pyrolyzes on the surface of the substrate, and subsequently forming the desirable materials. Minimal gas phase reactions are involved in pyrolytic LCVD because the precursors are selected such that they do not absorb at the laser wavelength. In the case of carbon nanotubes growth by LCVD, metal nanoparticles on the substrate are heated by either direct laser irradiation or conduction of thermal energy from the hot substrate. This leads to synthesis of nanotube materials by growth mechanisms similar to conventional CVD. Drawbacks associate with past LCVD techniques include: (1) the inability to control the size of metal particle catalysts, and (2) difficulties associated with controlling laser-induced gas phase reactions which complicate for scale-up production [5] and may potentially lower nanotube quality by gas phase contamination. In addition, the preparation of oriented CNTs requires to start from well-defined, plain surfaces and to control the selectivity in carbon, the geometry (aspect ratio), the density of CNTs and the electrical conductivity at the interface with the substrate [6]. The density and the size of the catalytic metallic nanoparticles previously deposited onto the substrate mostly determine the subsequent CNTs density and size [7]. Now one of the main challenge in the preparation of CNTs-based devices to address catalytic particle of controlled size at a controlled location. Insofar many preparation and dispersion techniques of the catalytic nanoparticles have been described in the literature, including printing [8], electrochemical deposition [9], sputtering and evaporation methods [10]. The objective of this study is to determine the feasibility of using pyrolytic LCVD to grow carbon nanotubes at room temperature on a multiple-catalyst layer (Fe/Al/Cr) substrate. The catalyst particles are applied onto the substrate through Vacuum Evaporation System. The effects of the precursor mixture on the growth of carbon nanotubes by pyrolytic LCVD are investigated in detail.

scanning electron microscopy will be used to investigate of the carbon nanotubes and the metal catalysts deposited in this study.

2. MATERIAL & METHODS

The synthesis of carbon nanotubes in this study consists of two steps: (1) the deposition of catalyst material on the substrate, followed by (2) the actual synthesis of nanotubes by laser-induced chemical vapor deposition. The multi-metal layers were deposited through electron beam and thermal evaporation in the vacuum chamber with 10^{-6} bar on quartz substrates ($10 \times 10mm^2$). The multi-metal system consisted of an Cr underlayer with multi-layer metal catalysts on top. The Cr underlayer with a thickness of 5 kAº was deposited first, followed by 0.1 kAº thick of Al, and then 0.02 kAº thick of Fe. The substrate was put into a vacuum chamber, and then chamber was flushed with Nitrogen gas for 10 min and during experimentation, the gas ratio of C_2H_2 to H_2 was varied from 0.5:2 to 1:4 and the chamber pressure was 132 mbar during the growth. A 2-W continuous wave carbon dioxide (CO2) laser operating at a wavelength of 10.6 μm is used to heat the substrate. Plano/convex zinc selenide (ZnSe) lens are used to focus the laser beam on the substrate. Proper alignment of the laser beam and the substrate is performed with the aid of a low power He–Ne laser beam. Alignments of laser optics are inspected during each experimental set to ensure repeatability of experimental conditions for subsequent experiments. Finally, the substrate was irradiated with the laser for 60 s to heat the catalyst on the substrate locally. After that, laser irradiation was stopped and the substrate was moved to another point to be irradiated. The circular areas corresponding to the position of the laser spot in the growing process were investigated by scanning electron microscopy (SEM).

3. RESULTS& DICUSSION

Different carbon sources, including ethanol vapor (C_2H_5OH) and acetylene (C_2H_2), were investigated for the synthesis of CNTs using LCVD in conjunction with the substrate described above. Among these gases, CNTs have only been obtainable with acetylene, to date. In the studies of CNT synthesis ,It was pointed out that: (i) backside laser irradiation as opposed to the commonly exercised front side irradiation of the substrate was one of the key factors for the successful growth of CNT patterns, (ii) the use of a Cr thermal layer on transparent quartz to enhance a uniform heat distribution within the laser spot was another central factor, and (iii) an Al buffer layer that prevents catalyst sintering was important in fabricating uniformly distributed CNTs. In the present study, a multiple-catalyst layer consisting of thin

Fe/Al/Cr layers (0.02/0.1/5 kAº) and the backside irradiation configuration were utilized. The relatively thick Cr layer was deposited as a thermal layer that provides uniformly distributed heat to the upper catalyst layers as the laser beam irradiates this Cr layer, whereas the Al layer was added to promote CNT growth because without the Al layer CNTs of only very poor density were produced. Although it was reported that Al assisted the formation of an effective catalyst (Fe) during CNT growth [11], its role in the present substrate configuration requires further research. It should be noted, however, that without either of the Al or Cr layer no CNT could be achieved.

In case of LCVD processes, the role of hydrocarbon gas (acetylene) is interconnected to both the laser reactions and the CNT growth. The local growth of nanotube is produced under increasing growth temperature of the laser irradiated substrate .Acetylene absorbs the laser radiation due to the resonant absorption at the CO_2 laser emission wavelength (10.6µm).Thus, due to the heating of substrate and gas mixture, the dissociation threshold at the gas-substrate interface could be reached.

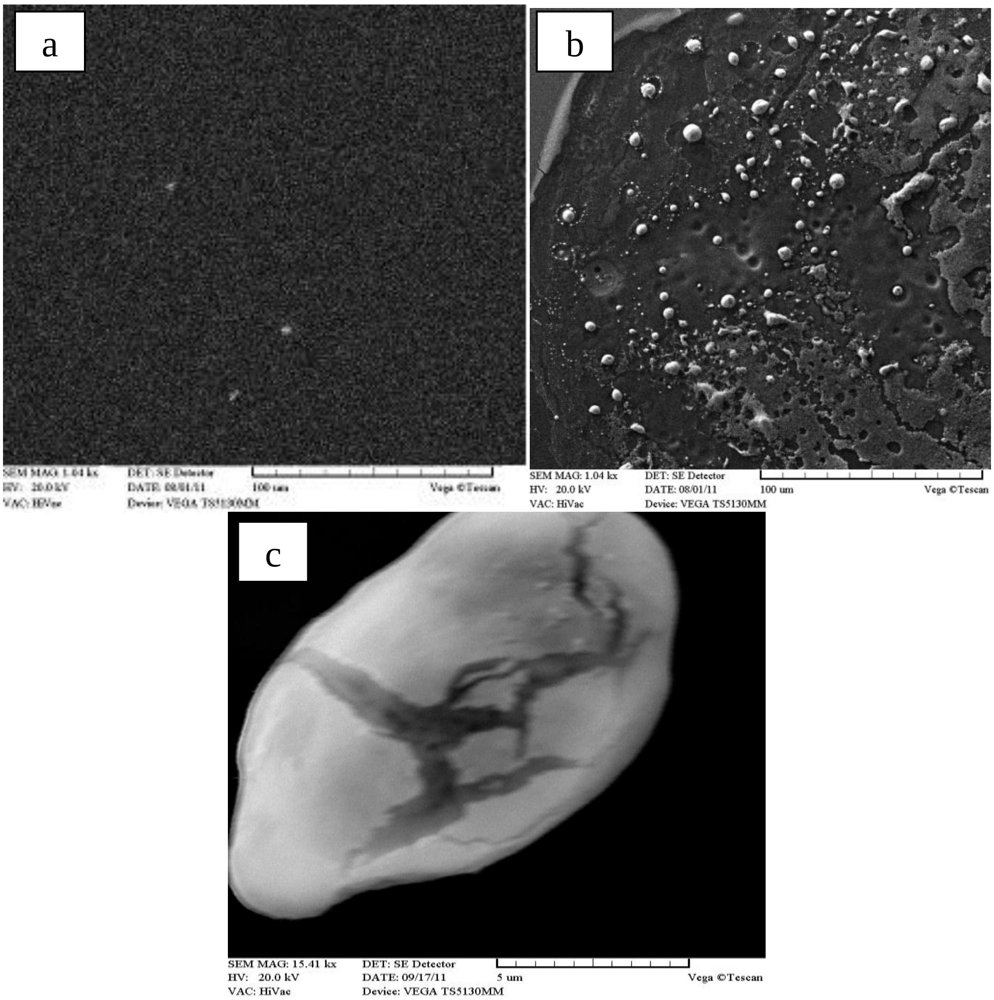

Figure 1. (a) SEM image of CNTs synthesized by slow heating. Power: 2W (b) SEM image of CNTs synthesized by step-input power. (c) Magnified view of the sidewall of the CNTs shown in (b). Power: 2W.

The growth rate of nanotubes depends on the hydrocarbon decomposition i.e. on the number of hydrocarbon radicals impinging on the catalyst surface. Different types of radicals are expected to have different decomposition rates. In the acetylene system, acetylene has the low dissociation energy [12]: DH298 [HCC–H] = 133.32 kcal/mol. It is considered that acetylene has a high influence on the CNT growth conditions, especially on the inner and outer diameter dimensions and on the decoration with nanoparticles [13]. Although the role of acetylene for nanotube growth is essential especially in LCVD [14] but also in thermal CVD processes (temperature range 550– 950 ºC) and even in plasma assisted CVD [15].

For this study, mixed gas C_2H_2/H_2 (0.1 slm/0.4 slm) and (0.05 slm/0.2 slm) was selected for growth the CNTs. The morphology of the CNTs, their dimensions and orientation was examined using SEM. Figs. 1a and c show representative SEM images of the samples, in general indicating the presence of CNT structures.

To examine the effects of heating rate and the gas ratio on the growth of CNTs, growths were investigated based on two temporally different irradiation modes and the gas ratio , including: (i) a ramp-heating mode in which the laser power was linearly increased to the power level required for CNT growth, equal to 2W and the gas ratio of C_2H_2 to H_2 0.5:2, for the present experiments, within a duration of 60 s, as shown in figure 1(a); and (ii) a step-heating mode in which the laser light instantly irradiated the substrate at the power of 2W and the gas ratio of C_2H_2 to H_2 1:4 for the present experiments, within a duration of 60 s , as shown in figure 1(b). For the ramp-heating experiment, CNTs wasnot obtained over the irradiated area, which failed to grow into a CNT (figures 1(a)). A possible reason that no CNTs were grown during this ramp heating is the deactivation of catalytic nanoparticles by slow heating; the formation of effective catalysts is highly dependent on preheating conditions for catalysts prepared by physical vapor deposition and nanoparticles of unfavorable size and shape could be formed through sintering in slow heating [16]. Another possibility is that in LCVD the reaction gases were fed into the chamber before laser heating, contrary to chamber CVD methods for which the source gases are supplied after the catalyst reached the optimal growth temperature. Thus, under slow heating conditions, nucleation and growth of CNTs and undesirable carbonaceous nanostructures may occur below the optimal growth temperature, but cannot reach the catalyst density and growth rate required for the growth of CNTs. Conversely, when the substrate was irradiated with an initial laser power of 2W, i.e. in step-heating mode, the growth of a CNT was possible, as shown in figure 1(c); laser irradiation lasted for 60 s at a power of 2W and the gas ratio of C_2H_2 to H_2 1:4.

Compared with the results for the ramp-heating case, growing CNTs became possible with the step-heating mode due to the fast heating of the catalyst layer with the laser. The rapid heating of the catalyst with an intense laser light is thought to lead to the generation of small Fe nanoparticles by minimizing the sintering time, thus providing a large number of active catalysts for CNT growth. Therefore, the nucleation and growth of CNTs may have occurred immediately on the active Fe catalyst particles under the fast heating condition, thereby leading to the subsequent growth of CNTs. Supporting this consideration, Li et al [17] suggested that, once metal nanoparticles nucleated carbon nanotubes, further nanoparticle sintering is repressed; the same situation may have happened to the catalytic nanoparticles for the CNTs grown in this study.

4. CONCLUSIONS

We reported the growth of CNTs on a multiple-catalyst layer using a single-step LCVD and flow rates of 0.1 and 0.4 slm for acetylene and hydrogen, respectively . From growth experiments using fast and slow laser heating of a substrate, it could be concluded that laser fast heating is one of the crucial factors enabling the observed growth of CNTs. This method can be easily applied for position-controlling CNT patterns at room temperature, with no need for annealing or catalyst prepatterning.

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