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Catalyst free, excellent quality and narrow diameter of CNT growth on Al_2O_3 by a thermal CVD technique

Nishant Tripathi, Prabhash Mishra, Bipin Joshi, Harsh, S.S. Islam *

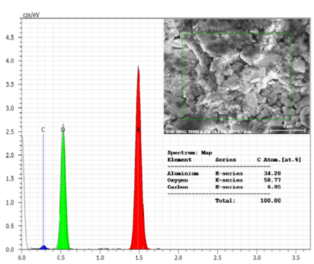
Solidstate Electronics Research Laboratory (SERL), F/O Engineering and Technology, Jamia Millia Islamia (Central University), New Delhi, India

HIGHLIGHTS

- Growth of CNTs was done on alumina (Al_2O_3) substrate without any metal catalyst.
- CNTs growth occurred in activated nucleation sights present on roughness of substrate.
- CNTs growth experiment was run in atmospheric pressure.
- Spectroscopic and microscopic studies confirmed the quality and structure of CNTs.

GRAPHICAL ABSTRACT

Graphical abstract shows the EDX results of grown CNTs on Al_2O_3 substrate. It clearly shows the presence of carbon, oxygen and aluminum in the sample material. The atomic percentage of C, O and Al are 6.95%, 58.77% and 34.28% respectively. The presence of aluminum and oxygen elemental contents confirmed that only Al_2O_3 along with CNTs is present on the grown sample.



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ABSTRACT

We report another unconventional growth of carbon nanotube (CNT) growth directly on flat alumina substrate (Al_2O_3) where neither any metal particle is used as a catalyst nor any supporting layer to facilitate its growth. All reactions are performed in atmospheric pressure in thermal CVD chamber. The diameter distribution is found 6–8 nm. The CNTs are characterized using HRTEM, HRSEM, micro-Raman and EDX analysis. The I_D/I_G ratio in Raman spectra and TEM picture ascertains that the CNTs contain less defects and presence of amorphous carbon and other particles are nil within the CNTs structure.

1. Introduction

Carbon nanotubes (CNTs) are known for outstanding superior electrical, mechanical, and electronic properties and because of these properties, considerable interest has been generated within the research community to undergo an in depth study to explore its physical and chemical properties leading to commercial applications for mankind. The applications are in many fields such as probes for atomic force microscopy [1,2], batteries [3], hydrogen storage [4,5], transistors [6–9], chemical and biological sensors [10–13], humidity sensor [14] flat panel displays [15], nanoelectronic devises [16] and field emitters [17,18]. But the major hurdles in view of its commercial applications came in due to its growth related issues such as poor control on its chirality – a decisive factor whether the CNTs will be metal or semiconductor, presence of carbonaceous and catalytic impurities causing poor electrical and electronic properties, and lump/bundle formation leading to poor dispersion in the as-grown CNTs. Fabrication of CNTs with a specific chirality is still a distant dream although the other issues have been solved. For batch fabrication, either we use a single nanotube with specific chirality followed by high cost nanomanipulation [19] or use aligned/random CNTs forest taking the average properties of CNTs [19]. The latter one is cheap, reliable, and involve low cost fabrication process, so that they can be

* Corresponding author. Tel.: +91 11 26980532.
E-mail address: sislam@jmi.ac.in (S.S. Islam).

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employed directly in their potential application areas [20]. Further improvement of nanotube properties is always desirable but the approaches are limited in the area of synthesis and post treatment on the CNTs.

To meet the demand of these potential applications, various CNTs growth methods have been evolved such as laser ablation [21], arc discharge [22,23], pyrolysis [24], thermal chemical thermal deposition (TCVD) [25,26] and plasma enhanced chemical vapor deposition (PECVD) [27,28]. In all these techniques the CVD method is capable in synthesis of high quality, high purity and high yield CNTs with controlled structure such as diameter, length and chirality on large scale. Due to these remarkable advantages of the CVD method vis-à-vis other techniques, it has gained much fame around worldwide researchers. However, for obtaining good quality of CNTs in practice, tuning of growth parameters is an essential requirement. Among which catalyst engineering such as type of catalyst, depositing technique of catalyst, etc., must need optimization because it has been inferred by several research works that the dimensions, morphology, yield and chemical composition of CNTs heavily depend on it [29,30]. Iron group metal particles (Fe, Ni, and Co) are mostly used as catalyst for CNTs growth, but these nanosize catalysts particles become a huge barrier in front of quality of CNTs as well as its electronics applications. Quality of CNTs is always a prime concern for device applications and it is very sensitive to growth temperature i.e. CNTs structural quality is good when growth temperature is high but vice-versa. If CNTs growth was performed at high temperature then the following things may occur: (1) metal catalyst particles agglomerate and become large resulting in increase of diameter of CNTs, (2) metal catalyst particles remain in CNTs which create distortion in actual characterization of CNTs, and (3) such type of catalysts particles also affects the thermal stability and magnetic properties of CNTs. Besides, for using grown CNTs with metal catalyst in electronic applications, a purification process for CNTs is required and it is a very difficult process itself and purification also creates defects in its structure. So metal catalysts particles are not compatible for CNTs applications. Therefore, growth of CNTs without metal or any other catalyst has become a challenging task for research community. Recently, it has been reported from some groups that some non-metals also worked like catalysts such as sputtered SiO_2 particles [31] and silica nano particles generated by random scratches on SiO_2 substrates [32]. In this report we demonstrate a simple and low cost technique to grow CNTs without catalyst and even without supporting base layer. We had grown CNTs on non-metallic flat alumina (Al_2O_3) substrate. Since in many case we are using an alumina layer on Si wafer as a supporting layer, therefore, it is quite compatible with CNTs based devices. Because alumina is a non-metallic, so there is no chance of metal particles remaining on as grown CNTs or on substrate and also that the melting temperature of alumina is extremely high so we get the solution of the above mentioned problem with metallic catalyst. As grown CNTs are analyzed by HRTEM, HRSEM, micro-Raman, and EDX studies which confirms the growth of high quality CNTs in the diameter distribution 6–8 nm.

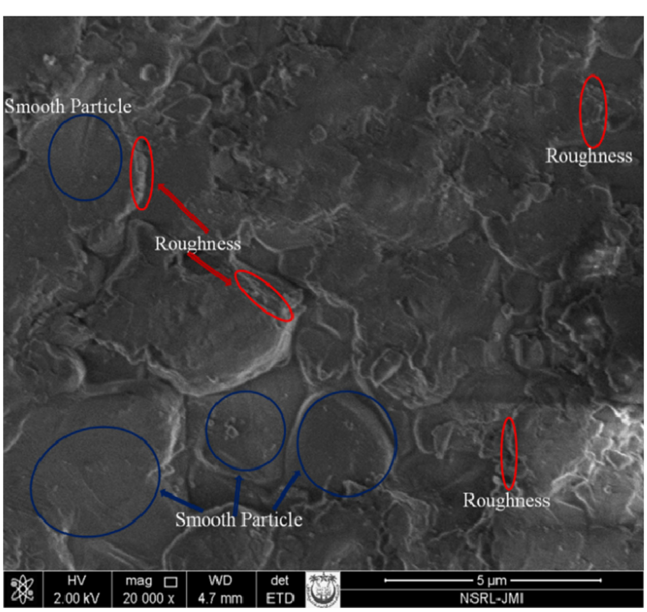

Fig. 1. FESEM image for surface morphology of alumina substrate.

2. Experiment

CNTs growth was performed on a 5 mm × 5 mm flat alumina (Al_2O_3) substrate. Before CNTs growth, we rinse the wafer with DI water and then clean the wafer by ultrasonicator in Iso Propile Alchohal (IPA) for 5 min. Then the wafer was treated by a oxygen plasma treatment for 5 min using a plasma treatment system (Diener Electronic Gmbh Germany) prior the wafer was ready for CNTs growth. After that, the wafer was placed in a quartz reactor of CVD system, and the heating process of reactor starts in the presence of Ar gas with 60 sccm constant flow rate. When temperature of reactor reached at 800 °C, CNTs were grown using acetylene (C_2H_2) gas with 20 sccm flow rate in addition to Ar gas with 60 sccm flow rate for 10 min. After 10 min, C_2H_2 flow was stopped and furnace turned off. For securing the grown CNTs from burning at such a high temperature, Ar flow was continued till the furnace cooled down to room temperature. The entire growth process was conducted under atmospheric pressure. After cooling, the sample was unloaded for analysis. As grown CNTs were investigated by HRTEM (TEM, FEI Tecani F20), HRSEM fitted with EDS (FESEM, NOVA NANOSEM 450) and Micro-Raman spectrometer with 488 nm Ar^+ laser (LabRAM HR800, JY).

3. Result and discussion

Fig. 1 shows the FESEM image of flat alumina surface before CNTs growth, in which we can clearly see the roughness on alumina substrate with some smooth large particles. We can see the FESEM image of grown CNTs without catalyst on a flat alumina substrate in Fig. 2(a) and (b) shows its magnifying picture. In these pictures, we can observe that a horizontal network of CNTs grown on whole alumina substrate except the above mentioned smooth large particles, which was a solid evidence for catalyst free CNTs growth. The proposed reason behind such type of CNTs growth is roughness of alumina substrate. Roughness of alumina substrate or its fluctuating surface provides the activated nucleation sites for initiating the CNTs growth process and alumina itself catalyzed the decomposition of hydrocarbon [33] and hence growth of CNTs on flat alumina substrate takes place. One more thing that large smooth particles situated on flat alumina substrate (see Fig. 1) left from the CNTs growth because on the surface of these particles no roughness is found and hence no nucleation sight is present on these particles. For investigation of grown CNTs, TEM characterization has been carried out and shown in Fig. 3. It is found that all CNTs are multiwall in structure with diameter distribution in the range of 6–8 nm. Raman spectra for grown CNTs were also collected and shown in Fig. 4. We can observe two important peaks one is D band at 1348 cm^{-1} and another is G band at 1587 cm^{-1}. Sharp high peak of G band and small peak of D band shows that grown CNTs have good crystallinity because ratio of intensity of D band and G band define the quality of CNTs. Fig. 5