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A Facile Solution Based Nickel Deposition Method for the Formation of Vertically Aligned Carbon Nanotubes

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Abstract

A novel chemical solution deposition approach is reported for the deposition of nickel catalyst, which is a required step for the growth of carbon nanotubes (CNTs). In this work, after catalyst coating, vertically aligned CNTs have been grown on the silicon oxide and silicon surfaces. The results were studied using field emission scanning electron microscopy (SEM), Raman and X-ray diffraction. This technique has a high selectivity over the size of the catalyst nanoparticles, which results in the simple controlling of the average diameter of grown CNTs in the range of 30 to 150 nm. In addition, this approach leads to a more conformal coating on the surface of the sample in comparison with traditional vacuum-based deposition techniques, enabling the growth of CNTs on highly rough surfaces. The proposed catalyst deposition technique is a fast, inexpensive and simple Nickel catalyst deposition method that can significantly facilitate the growth process of CNTs.

Keywords: Deposition, Solution, Ni, CNT, Catalyst

Introduction

Carbon nanotubes (CNTs) are one of the allotropes of carbon that because of their extraordinary properties, have found many applications in modern technologies [1]. Although a long time has been passed since their discovery in 1991 [2], a considerable research is still ongoing on their fabrication process [3]. There are several techniques for the growth of CNTs such as chemical vapor deposition (CVD), arc discharge and laser ablation, which are mainly based on catalytic enhanced formation of CNTs [4–6]. The CVD methods for CNT growth are known to be simple and more reproducible [7]. In these methods hydrocarbon precursors such as CH_4 [8], C_2H_2 [9], CO [10] and benzene [5] are decomposed and the growth of CNTs is obtained with the aid of catalyst nanoparticles on the surface of the sample [11].

Among different methods of CNT growth, plasma enhanced chemical vapor deposition (PECVD) has gained much attention due to enabling the growth of CNTs at very low temperature [12]. Transition metal catalysts such as Ni, Co, Fe and Mo are used as the main catalyst materials for CNT growth with PECVD technique, that can be deposited on the sample using physical evaporation systems or incorporating chemical solution coatings [13–23].

During the CNT growth using PECVD, the width of CNTs seems to be related to the catalyst layer thickness. Usually thinner catalyst films result in smaller catalyst grains and consequently smaller CNT diameters [23]. Since the deposited catalyst layers are not usually in the form of nano grains, an additional step is necessary to obtain the desired catalyst nanoparticles on the surface of the sample. In a PECVD process, the sample coated with the catalyst layer is first exposed to H_2, NH_3 or some inert gases plasma in order to facilitate the formation of the catalyst nano grains. Then the growth process starts by exposing the sample to the plasma in the presence of hydrocarbon containing gases [16,18,20,22] . There are several reports such as the work of Delzeit et al [14–17] that have used a metal such as aluminum under the catalyst layer, which helps to form catalyst nanoparticles on the surface without the need to an extra chemical pretreatment step.

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As stated before, besides the physical deposition processes, the other approach for catalyst coating is chemical solution method, which is usually not preferred over the evaporation deposition techniques because of their drawbacks such as being very time consuming and cumbersome [7]. A typical chemical solution coating process includes several steps as dissolution, stirring, annealing, drying, separation, precipitation and cooling [6,7]. Carnes et. al reported the use of $NiCl_2$ and NaOH solution for NiO formation [25].

In this paper, we have used this $NiCl_2$/NaOH solution dissolved in ethylene glycol to realize Ni islands as the catalyst in a conformal fashion on silicon substrates and on previously grown nanotubes. Besides the simplicity of this method in comparison with typical catalyst coating processes, it has high selectivity of particle size and consequently the nanotubes diameter. By applying this solution-based approach, vertically aligned CNTs have been grown with controlled average diameter. High conformality of the catalyst coating is also achieved in this method which enables us to coat the external sidewalls of the previously grown CNTs with Ni catalyst nanoparticles.

Powder X-ray diffraction (XRD) measurement was performed on a PANalytical X'Pert Pro MPD X-ray diffraction instrument using CuKα radiation. Hitachi S-4160 field emission scanning electron microscopy (FE-SEM) was used to determine the morphology of the branched CNTs. Raman spectroscopy have also been employed to study the structure of CNTs grown with solution based Ni catalyst deposition approach.

Experimental Details

For our experiments, P type silicon wafer with the orientation of <100> has been used. In the fabrication process, first the surface of the wafer is cleaned using RCA#1 solution (NH_4OH : H_2O_2 : H_2O ; 1 : 1 : 5). When a SiO_2 layer is needed, the cleaned silicon wafer is transferred into oxidation furnace (at 1050°C) with O_2 atmosphere for two hours, which leads to about 200 nm growth of the silicon oxide layer on the wafer.

The solution used for chemical deposition of Ni catalyst layer is the mixture of $NiCl_2.6H_2O$ in ethylene glycol (EG) and NaOH aqueous solution. This solution results in Ni particle coating on the surface, where with an additional CNT growth process, vertical nanotubes are resulted on the surface of the sample. The size of nanoparticles can be controlled by adjusting the concentration of the solution, and consequently the diameter of CNTs can be controlled. We tested three distinct concentrations for the formation of Ni nanoparticles as follows: for sample No. 1, 4.5mL from 1M NaOH aqueous solution was dissolved in 50 mL of 9 mM nickel chloride [$NiCl_2.6H_2O$] in EG solution; for sample No. 2, 9mL from 1M NaOH aqueous solution was dissolved in 50 mL of 18 mM nickel chloride [$NiCl_2.6H_2O$] in EG solution; and finally for sample No. 3, 18mL from 1M NaOH aqueous solution was dissolved in 50 mL of 36 mM nickel chloride [$NiCl_2.6H_2O$] in EG solution. These experiment are shown in table 1. The NaOH solution acts as reducing agent and the reaction rate is dependent to its concentration. We tried to test all the experiments in the same reaction rate and reaction time. Therefore we set the NaOH concentration constant.

Table 1: Solution method parameters for three different experiments

Sample no.	NaOH : 1M	Nickel chloride [NiCl2.6H2O] in EG solution : 50 mL
1	4.5 mL	9 mM
2	9 mL	18 mM
3	18 mL	36 mM

In order to deposit Ni particles on the surface of the sample, first the wafer is completely soaked in a petri dish containing 50 mL Ethylene glycol. Then the sample is moved to $NiCl_2$ solution with continuous stirring at room temperature. Consequently, the NaOH solution is added to the $NiCl_2$ solution according to table 1. After 30 minutes the sample was removed from the mentioned solution and dried at 120 °C in an oven. After coating the sample with Ni particles, it was transferred to a DC-PECVD system to grow CNTs on its surface. The PECVD process used for CNT growth was as follows: the process starts with an annealing step in which upon heating to 680 °C under a hydrogen atmosphere with flow rate of 20 sccm, the Ni catalyst is activated. Then, to initiate the growth of carbon nanostructures, C_2H_2 gas with the flow rate of 7 sccm is added to the chamber, and a DC plasma with 600 V and 4.5 mA/cm^2 is applied on the sample for 10 minutes. At the end of the growth period, samples were slowly cooled within the chamber, under H_2 gas environment. It is worthwhile mentioning that if electron beam evaporation technique is used for Ni catalyst coating on the sample (instead of this solution based coating), then an additional step of hydrogen plasma was needed between the annealing step and C_2H_2 plasma, to facilitate the formation of nano grains of catalyst on the surface enabling the growth of CNTs in the subsequent step. However the solution based Ni coating described above results in grains of Ni catalyst on the surface of the sample, without an additional pretreatment step of nanoparticle formation.

Results and Discussion

The reaction involved in this solution based Ni nanoparticles preparation is as follows:

$$NiCl_2\ (aq) + NaOH\ (aq) \rightarrow NiClOH\ (s) + NaCl\ (aq) \qquad (eq.1)$$

According to eq. 1, the mentioned solution will result in the formation of NiClOH on the sample. When the sample is transferred to the PECVD system for growth of CNTs, while thermal annealing step in the hydrogen atmosphere, these reactions will occur:

$$NiClOH + 0.5\ H_2 \xrightarrow{annealing} NiOH + HCl \qquad (eq.2)$$

$$NiOH + 0.5\ H_2 \xrightarrow{annealing} Ni + H_2O \qquad (eq.3)$$

As can be seen in these two equations, in the thermal annealing process, NiClOH is finally reduced to Ni through an intermediate product of NiOH.

XRD was used to obtain the crystal structures of samples. Figure 1 shows the XRD pattern of the solution approach deposition before and after annealing. NiClOH peaks can be seen in the XRD result of sample before thermal annealing, while after annealing process, there is no evidence of NiClOH peaks, but Ni peaks are apparent in the pattern [27]. The crystallite size of the as-prepared Ni was calculated from the major diffraction peaks of the Ni using the Scherrer formula, to be about 70 nm for (1 1 1) Ni nanoparticles. XRD results confirm that the solution based approach results in formation of NiClOH on the sample that during hydrogen thermal annealing in PECVD system will finally reduce to Ni catalyst. This Ni can be used as the catalyst for growth of CNTs, and therefore this solution based approach can finally result in Ni catalyst coating on the sample.

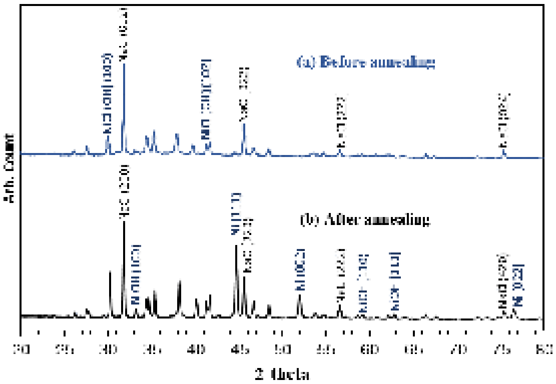

Fig. 1- XRD result of as-prepared product (a) before, and (b) after annealing at 680°C. Ni peaks (shown by dashed curves), are clearly observed in the annealed sample.

Figure 2 shows the diameter distribution of CNTs grown with specified concentration of solution. It was calculated using the related SEM images and a MATLAB code written for this purpose. Different parts of this figure are related to various concentrations in the solution based Ni catalyst deposition method. It can be seen that the average diameter of CNTs has been controlled with solution concentration. Diameter size distribution of CNTs with mean diameter of 35 nm can be seen in part (a), and parts (b) and (c) correspond to CNTs with average diameter of 53 and 98 nm respectively. Thus by this method, CNTs can be easily grown with desired diameters just by setting proper concentrations of the solution, while it is a difficult issue in the physical catalyst preparation techniques.

Figure 3 collects the SEM images of CNTs grown with our solution based Ni coating method. Different concentrations in the solution (explained in the previous section) resulted in different diameters of grown CNTs. Parts (a) to (d) of this figure show CNTs grown on SiO_2 substrate. CNTs with average diameter around 35 nm (part (a)), 53 nm (parts (b)), and 98 nm (part (c)) can be seen in this figure. For comparing the results on silicon and SiO_2 substrate, SEM images of 50 nm diameter CNTs on Si wafer is shown in parts (d) of the figure 3. By comparing parts (d) with (b)-(c), it is concluded that on SiO_2 substrate the growth of CNTs has a much more uniform distribution than on the silicon substrate. This difference is believed to be due to hydrophilic nature of SiO_2 which leads to a better conformal distribution of Ni particles.

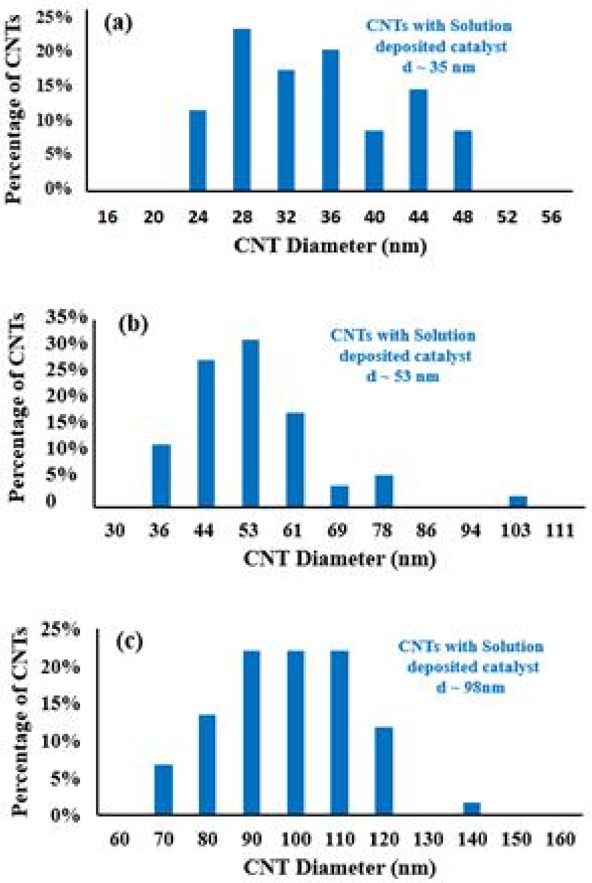

Fig. 2- Diameter distribution of CNTs grown with different concentrations of the solution according to table 1 (a) sample no.1 (b) sample no.2 and (c) sample no.3

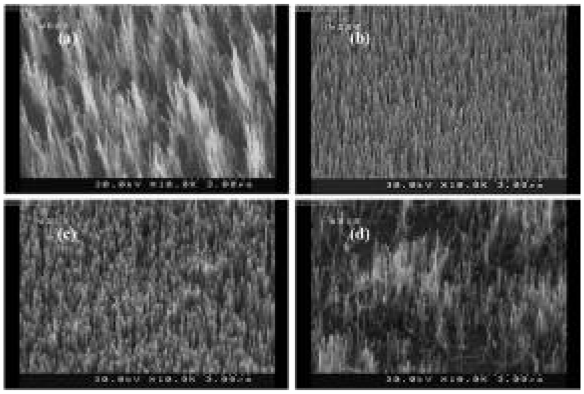

Fig. 3- CNT growth on solution based Ni catalyst coated SiO2 substrate (a) 35 nm, (b) 53 nm, (c) 98 nm. It can be seen that CNTs are grown uniformly in a wide range on the substrate. (d) CNT growth on solution based Ni catalyst coated Si Substrate.

The Raman spectra of grown CNTs with this solution based Ni catalyst deposition are shown in figure 4. The sample used for this analysis has an average diameter of 53nm. The G/D ratio in the Raman spectra is believed to be related to the amount of sp^2-hybridized carbon versus the amount of disordered ones, which is a measure of CNT structural quality [26]. The results for CNTs with electron beam deposited Ni is also depicted in part (b) of this figure. The G/D ratio for CNTs with solution prepared catalyst is 0.6 while this value is 0.43 for CNTs with electron beam deposited Ni catalyst. This shows the better structural quality of CNTs obtained with solution based catalyst deposition technique. In our experiment the average diameter of CNTs are smaller in the case of solution based Ni catalyst, in comparison with E-Bram deposited Ni. It is reported that smaller diameters of CNTs would result in higher FWHM of the D and G peaks that is in agreement with figure 4 [28].

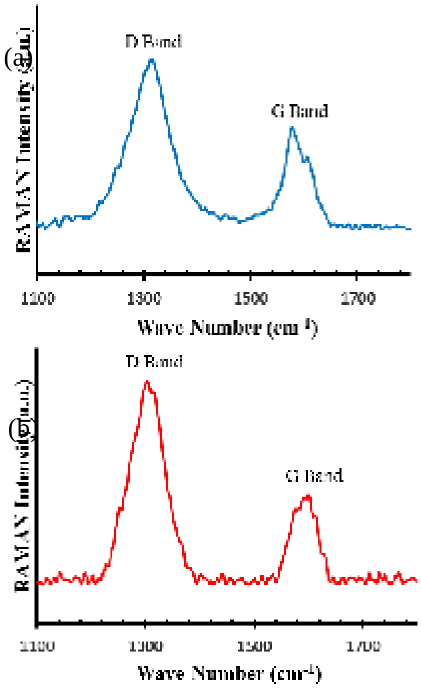

Fig. 4- Raman spectroscopy of CNTs. (a) CNTs with solution based catalyst preparation. G/D=0.6 for this case. (b) CNTs with electron beam catalyst deposition. G/D in this case is 0.43.

Short time catalyst preparation can be regarded as an advantages of this solution based method in comparison with many physical based methods such as electron beam evaporation. Time consumption for catalyst deposition with our electron beam evaporation system is about 8 hours while the time required in the mentioned solution based method is about half an hour. Another advantage of this solution approach compared to physical method, is the ability to deposit the catalyst on the walls and the surface of the structures even with high aspect ratios. To show this, we applied this method to grow CNTs on the structures with vertical walls. Figure 5 collects SEM images related to the growth of CNTs on the sample with silicon rods. For this experiment the surface of the silicon wafer was coated with a Cr layer using electron beam evaporation system and then was patterned with an additional photolithography step to form arrays of Cr micro-disc on the surface of silicon wafer. A consequent silicon vertical etching process results in formation of micro cylinders on the surface, as can be seen in figure 5(a). Next the Cr masking layer was etched and the sample was coated with Ni particles using our solution based approach. Performing CNT growth process on this sample results in SEM images of parts (b) and (c) of this figure. It can be seen that although the walls were vertical, still some CNT growth can be seen on the surface of these vertical walls, indicating the ability of the solution method for Ni coating of the sidewalls. For comparison the result of CNT growth on the similar silicon patterned sample but with electron beam Ni coating is shown in part (d) of Figure 5. It is evident that no CNT growth occurred on the sidewall surface of the sample in this case. So it can be concluded that the solution based catalyst coating is highly more conformal in comparison with the physical evaporation coatings. As a result, in the cases we want to cover all the surface of a sample with some rough features on it, this solution based method is more suitable than physical evaporation methods with smaller angles of deposition.

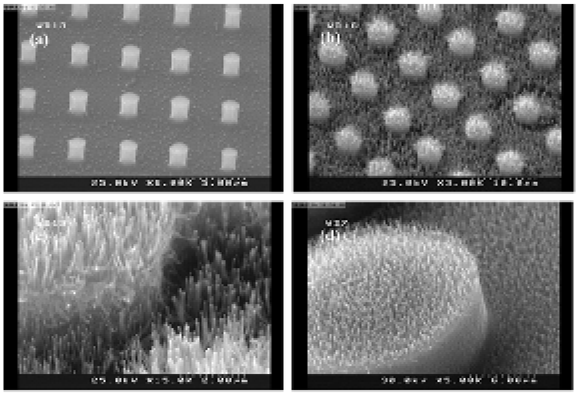

Fig. 5- (a) Fabrication of silicon micro cylinders using photolithography and silicon vertical etching process. (b) and (c) the results of coating the sample in part (a) with Ni catalyst using the solution approach and performing CNT growth process on it. (d) For this sample electron beam evaporation system was used for deposition of the Ni catalyst layer. No CNT has grown on the vertical walls.

Conclusion

A novel solution based approach is reported for deposition of Ni catalyst layer which is a fast, simple and inexpensive method. The solution is composed of nickel chloride in EG and NaOH solution, and the immersion time required for the Ni deposition on the samples is around 30 minutes. This catalyst coating can be used for growth of vertically aligned CNTs using a PECVD system. By setting the proper concentration of the solution the diameter of the CNTs can be controlled in the range of 30 to 150 nm. This deposition approach is highly conformal and enables the growth of CNTs on rough surfaces. The proposed catalyst deposition method can significantly facilitate the growth process of carbon nanotubes.

Acknowledgments

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