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Diamond & Related Materials 14 (2005) 744–748

DIAMOND AND RELATED MATERIALS

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Selective growth of carbon nanotubes on nickel oxide templates created by atomic force microscope nano-oxidation

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Abstract

The selective growth of carbon nanotubes on nickel oxide templates of square blocks of size 2×2 μm^2 on Si by a microwave-heated CVD has been successfully demonstrated. By applying a negative bias to a conductive tip, nickel oxide patterns were first created by the process of nano-oxidation. The unoxidized nickel film was then removed using a wet chemical etch technique, thereby forming nickel oxide templates over which the carbon nanotubes were grown. We also obtained single carbon nanotubes on nickel oxide nanodots that have diameters as small as 100 nm. The selective growth of CNTs over nickel oxide templates could be also fulfilled on not nickel-etched substrate by appropriately controlling the growth temperature and growth time.

Keywords: CVD; Carbon nanotubes; Atomic force microscope; Nano-oxidation

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1. Introduction

Since their discovery, carbon nanotubes (CNTs) have been the focus of extensive research activities due to their extraordinary properties [1]. In many applications, selective growth of CNTs is an essential issue. Photolithography [2], electron-beam lithography [3,4], micro-contact printing [5], shadow masking [6], synchrotron radiation lithography [7], nanosphere lithography [8], etc. have been utilized to create catalytic templates for the desired selective growth of CNTs. Among these techniques, electron-beam lithography has been used most often to generate catalytic patterns of sizes from sub-micron down to several tens of nanometer. Recently, scanning probe lithography has proved to be a highly promising technique for nanofabrication at the nanometer scale [9]. In particular, extensive work has been carried out to explore the potential of nanolithographic writing using the atomic force microscope (AFM) nano-oxidation technique [10–12]. In this work, we follow the merit of AFM nano-oxidation patterning technique to generate Ni oxide (NiO_x) templates for selective growth of CNTs. Our approach is based on local oxidation of a thin nickel (Ni) film to form NiO_x pattern using an atomic force microscope (AFM) tip and subsequent selective etching of the unoxidized nickel [13]. Realization of selective growth of CNTs on the NiO_x templates was then achieved with a microwave-heated chemical vapor deposition (MH-CVD) process [14,15]. The selective growth of CNTs on NiO_x templates could be also fulfilled even with the Ni unetched by controlling the growth temperature and growth time. Advantages of the present method include nanoscale resolution, relatively low cost, and ease of operation.

2. Experimental

Fig. 1 shows the schematic process for our selective growth of CNTs on NiO_x templates created by AFM nano-oxidation patterning technique. First, a 15 nm thick Ni film was deposited using electron beam evaporation onto a p-type Si(100) substrate which was coated with a 1-μm silicon dioxide buffer layer. The nano-oxidation of Ni was then

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doi:10.1016/j.diamond.2005.01.038

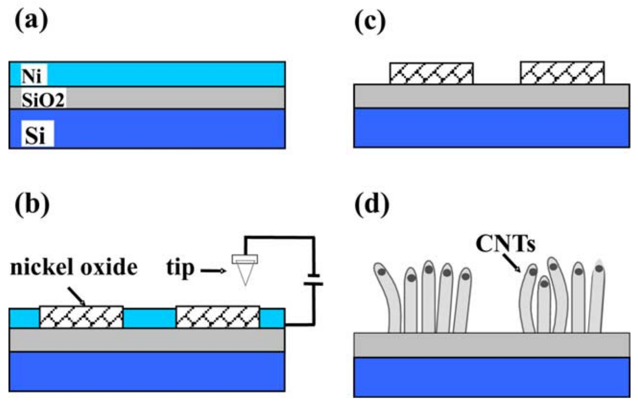

Fig. 1. A schematic process flow for the selective growth of CNTs on NiO_x templates created by AFM: (a) the initial layered structure, (b) the AFM nano-oxidation, (c) the etching of nickel, and (d) the growth of CNTs.

performed in a commercial AFM (Smena-A, NT-MDT, Russia) under ambient condition with humidity of around 50%. For oxidation, a negative bias was applied to the tip with the sample grounded. Following the oxidation, the sample was dipped into a solution of 14% nitric acid to selectively remove the unoxidized nickel. More details on the nano-oxidation of nickel can be found in Ref. [13].

The as-processed silicon substrate containing NiO_x templates was mounted onto a silicon carbide (SiC) susceptor using silver paste and then loaded into the MH-CVD chamber for the growth of carbon nanotubes. The SiC susceptor here was used to absorb microwaves, thereby heating the substrate very fast. A schematic of the MH-CVD apparatus can be found in Ref. [14]. For this study, pure methane (CH_4) with a flow rate of 200 sccm was used as the carbon source, and the chamber pressure was maintained at 1 atm during preheating and growth periods. The methane gas was introduced into the chamber prior to the onset of microwave heating. It generally took about 5 min to heat a Si substrate from room temperature to the growth temperature. For this study, two growth temperatures of 700 and 750 °C were utilized. Once the growth temperature was reached, it was held for 10 min. Then the microwave power was shut off and both the inlet and outlet for methane gas were closed, too. The cooling to ~100 °C took about 10 min. The morphology and structure of the as-grown CNTs were examined using scanning electron microscopy (JSM-6500F, JEOL, Japan) and Raman spectroscopy (He–Ne laser, Renishaw), respectively.

3. Results and discussion

With a tip bias of -8 V, a nickel-oxide square with a size of $1.8\times1.8\ \mu\text{m}^2$ was generated, and the scanning electron microscope image after removing unoxidized Ni is shown in Fig. 2(a). The NiO_x pattern is around 65 nm higher than the unoxidized region. To verify if the unoxidized Ni was completely removed by the etching process, Auger electron spectroscopy measurements were performed on the pattern and the surrounding region. The results indicated a successful removal of the nickel without affecting the oxide patterns [13]. The SEM image of CNTs so grown at 700 °C on this oxide template is shown in Fig. 2(b). As can be seen clearly in the image, most CNTs have the nickel catalysts at their ends, but some have nickels at their bases. The tip growth mode is therefore preferred over the base growth mode, which is consistent with our previous work using nickel as the catalyst [14,15]. An array of 3×3 nickel oxide squares of size 2 ìm were similarly fabricated, and the SEM images prior to and after the CNTs growth at 700 °C are shown in Fig. 2(c) and 2(d), respectively. The diameter and length of CNTs shown in Figs. 2(b) and 2(d) are in the range of 50–80 nm and 1–2 ìm, respectively, and the growth rate was estimated about 0.2 μm/min. Apparently, the present approach can be used effectively for a selective growth of CNTs on Si.

It has been reported that a catalyst dot size of around 100 nm or less is essential for the growth of single nanotubes [3,4,16]. By using voltage pulses, nickel oxide nanodots with sizes of less than 100 nm have also been successfully fabricated [13]. For this study, a 4×4 nickel oxide nanodots array was generated with the application of -10 V, 50 ms pulses, and the SEM image of it after removing the

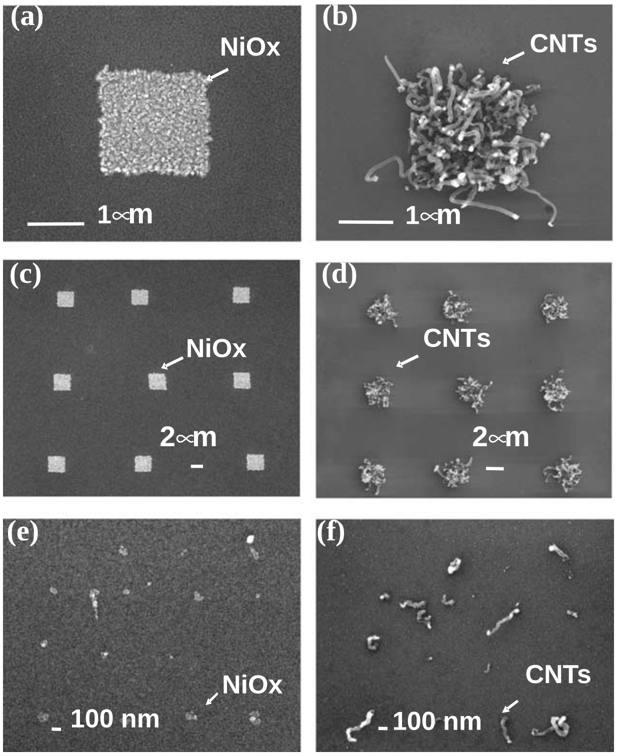

Fig. 2. SEM images of NiO_x templates with varying geometries: (a) a single square of size 1.8 μm, (c) a 3×3 array of 2 μm×2 μm squares, and (e) a 4×4 array of dots of ~90 nm in diameter. The corresponding CNTs grown on these NiO_x templates at 700 °C for 10 min are shown in (b), (d), and (f), respectively.

unoxidized Ni is shown in Fig. 2(e). Due to the small size of the oxide dots, some of them were etched away or moved to different positions. Single CNTs were then successfully grown at 700 °C over these oxide nanodots and the resultant SEM image is shown in Fig. 2(f). Because the NiO_x nanodots are of different sizes, the diameters and the lengths of CNTs also vary to some extent. With a better control of the nanodot size and an improvement in the growth conditions, the production of more uniform single CNTs can be expected.

To identify the role of nickel oxides during CNTs growth, energy dispersive x-ray spectrometry (EDS) measurements were performed on similarly produced oxide squares before and after growth. The growth time and the growth temperature were adjusted in this part of work to prevent complete formation of CNTs. Table 1 summarizes the EDS analysis results obtained on a NiO_x template of size 3×3 μm^2 before and after growth at 600 °C for 20 min. This EDS composition analysis indicated the presence of a large percentage of oxygen in nickel oxides before growth, but no trace of oxygen after growth. Based on this observation, a reasonable chemical route for the CNTs growth over nickel oxides is described as follows. The methane decomposes upon substrate heating into carbon and hydrogen gas. The hydrogen reacts with the oxygen in nickel oxides and the nickel is formed, which then facilitates the growth of Ni–CNTs complex. The argume.nt can be exemplified with the following reactions:

$$CH_4 \rightarrow C + 2H_2$$

$$NiO_x + xH_2 \rightarrow Ni + xH_2O$$

$$Ni + C \rightarrow Ni - CNTs.$$

In all the above results, a wet chemical etching after nano-oxidation was employed to remove the unoxidized Ni. It is possible, however, to skip this etching step and still achieve the selective growth of CNTs on NiO_x templates for the growth temperature of 700 °C. For this purpose, a portion of the unoxidized Ni was left by masking it with photoresist during the nitric acid etching. Therefore, both Ni and NiO_x templates appeared on the same Si wafer and therefore were subjected to the same growth condition. Fig. 3(a) shows the SEM image of the carbon film, which was grown at 700 °C for 10 min over the onoxidized Ni film. The image reveals only the existence of carbon-coated Ni particles and/or carbonaceous particles, in contrast to the CNTs found on the NiO_x templates as shown in Fig. 2. The high selectivity of growing CNTs on Ni oxide over Ni was thus confirmed. Nevertheless, once the growth temperature was increased to 750 °C but with the same 10-min growth time, CNTs could grow on both Ni and NiO_x templates, as confirmed from the SEM images shown in Fig. 3(b) and the inset, which were obtained from the CNT films grown on a Ni film and a NiO_x template of size 3×3 μm^2, respectively. It is also interesting to note in these images that the CNTs grown on the Ni film are much longer than those grown on the NiO_x template. A preferable growth of CNTs on Ni to NiO_x template is then suggested at the growth temperature of 750 °C, in contrast to the highly selective growth of CNTs on NiO_x templates at 700 °C.

It is worthy to investigate the underlying growth mechanism regarding the different growth rates for CNTs on Ni and NiO_x templates for different growth temperatures. The tip growth mode has been favored for our CNTs growth on Ni [14,15] and the present NiO_x templates. According to M. Chhowalla et al. [17], there are three steps for the growth of CNTs in the tip-growth mode. The first is the

Table 1
EDS analysis results obtained from a NiO_x template of size 3×3 μm^2 before and after growth at 600 °C for 20 min

Element	Before growth		After growth	
	Weight %	Atomic %	Weight %	Atomic %
C	-	-	38.96	63.18
Si	71.91	72.28	45.80	31.77
Ni	17.01	8.18	15.24	5.06
O	11.07	19.54	-	-

The “-” denotes the content of the element is under the detection limit of spectrometer.

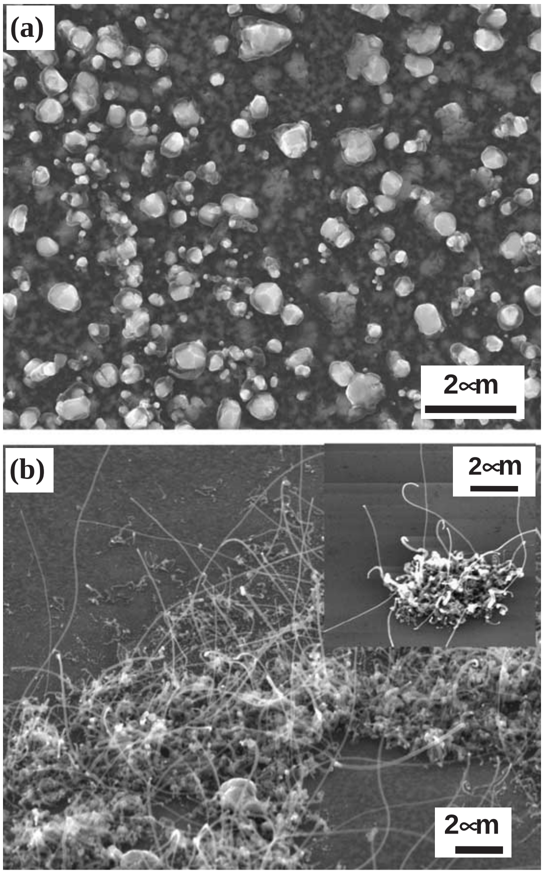

Fig. 3. SEM images of Ni films on not Ni-etched substrate after a 10-min nanotubes growth at (a) 700 °C and (b) 750 °C. The inset in (b) shows the SEM image of nanotubes grown on a NiO_x square template of size 3 μm at 750 °C for 10 min.

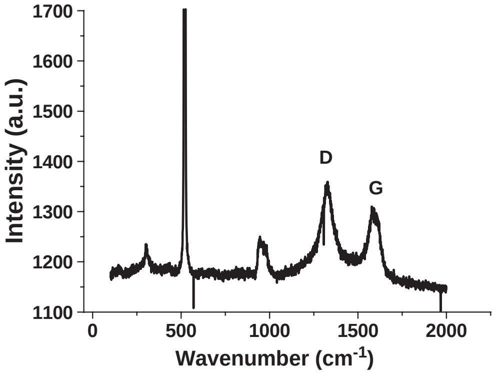

Fig. 4. Raman spectrum of nanotubes shown in Fig. 2(b) which were grown on a single NiO_x square template of size 1.8 μm at 700 °C for 10 min.

fragmentation of catalyst into nanoparticles or islands by annealing or sintering, the second is the decomposition of hydrocarbon radicals on the top of catalyst nanoparticles, and the third is the growth of nanotubes below the catalyst by carbon diffusion through the catalyst particle. In our MH-CVD process, the Ni film becomes fragmented around 500 °C, while the methane gas is supplied prior to the onset of preheating. Therefore, the Ni nanoparticles will be inevitably coated with a thin amorphous-carbon (a-C) overlayer during preheating, due to the insufficient energy supplied. This a-C overlayer then would defer the decomposition of methane gas on the surface of Ni nanoparticles, and the resulting dissociation of carbon species into the Ni nanoparticles through diffusion. The thickness of a-C overlayer is expected to be inversely proportional to the growth temperature, since an almost constant temperature-ramping time (~5 min) was used with our CVD process. Therefore, if the growth temperature is not high and/or the growth time is not long enough, carbon nanotubes would not grow. This may explain the formation of a-C overlayer coated Ni naoparticles at 700 °C but the growth of CNTs at 750 °C on Ni, as shown in Fig 3(a) and (b), respectively. The growth mechanism of CNTs on NiO_x templates is slightly different from that on Ni. As mentioned earlier, it is the Ni not NiO_x that is responsible for the growth of CNTs on NiO_x templates; that is, the NiO_x must be reduced first to Ni with the aid of hydrogen gas that is a product of methane decomposition, and then the three steps for the tip growth can take place. Although the time needed for a complete reduction of NiO_x to Ni at 700 °C was not well known, it is reasonable to assume a negligible formation of a-C overlayer surrounding the just reduced Ni during the preheating period. Therefore, CNTs can be produced on NiO_x templates at 700 °C for the same growth time of 10 min. The Raman spectrum of nanotubes shown in Fig. 2(b) is plotted in Fig. 4, in which D and G peaks are sharp and well separated, indicating the presence of negligible amount of a-C overlayer. If the growth temperature is high enough, say 750 °C, the a-C overlayer is also quite thin in the case of growing CNTs directly on Ni, which thus facilitates the growth of CNTs on Ni in a faster speed than on NiO_x templates, since in the latter case the reduction of NiO_x to Ni consumes some growth time.

4. Conclusions

In summary, a selective growth of CNTs at 700 °C for 10 min on NiO_x templates by a MH-CVD process has been successfully demonstrated. We could also obtain single carbon nanotubes grown over NiO_x nanodots that have diameter as small as 100 nm by the present method. The NiO_x templates were formed by AFM nano-oxidation and subsequent wet chemical etching of unoxidized Ni. The chemical route of the whole process is mainly attributed to the reduction of nickel oxide to nickel with the aid of hydrogen gas that is product of the methane decomposition. The selective growth of CNTs on the NiO_x templates could be also fulfilled at 700 °C even with not Ni-etched substrates. The much slower rate of growing CNTs on unoxidized Ni at 700 °C can be attributed to the formation of a-C overlayer around Ni nanoparticles formed during preheating stage. The present approach has the advantages of nanoscale resolution and easy operation, and can be valuable in the construction of CNTs-based nanoelectronic devices.

Acknowledgements

This work was supported by the National Science Council under Grant Nos. 92-2120-E-007-005 and 93-2216-E-007-033, and the Ministry of Education, Program of Academic Excellence under Grant No. A-91-E-FA04-1-4.

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