

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

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Abstract

We report the selective growth of carbon nanotubes (CNTs) on nickel oxide catalytic templates created by atomic force microscope nano-oxidation. Nickel oxide patterns are first produced on a nickel film by applying a negative bias to the tip. After removing unoxidized nickel, oxide patterns or nanodots with a smallest size of around 30 nm are successfully fabricated. Vertically aligned bunched or single CNTs with diameters of 30–80 nm are selectively grown on the oxide nanostructures by inductively coupled plasma chemical vapor deposition. It is also shown that the tube diameter can be effectively controlled by the dot size.

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1. Introduction

Due to their unique properties, carbon nanotubes (CNTs) have been the focus of extensive research activities since their discovery [1–3]. In particular, the selective area growth of vertically aligned CNTs [4] is of great importance for applications in field emission devices [5], vertical interconnects [6,7], and other novel devices. From this aspect, catalytic patterns for the CNT growth have been created by various techniques [4] including photolithography [8], e-beam lithography [9,10], micro-contact printing [11], shadow masking [12], ion beam modification [13], etc. Among these techniques, e-beam lithography is frequently used to generate sub-micron catalytic templates, and so far the best choice to achieve controlled nanoscale positioning of catalytic nanodots, which is imperative for the growth of single and isolated CNTs on desired locations.

In this Letter, we demonstrate a new approach for the selective growth of CNTs with nanoscale position control. The catalytic templates are made of nickel oxide created by atomic force microscope (AFM) nano-oxidation [14,15]. Successful growth of vertically aligned CNTs on the oxide templates has been realized by inductively coupled plasma chemical vapor deposition (ICP-CVD) [16]. In addition, single CNTs are also produced on oxide nanodots and their diameters can be regulated by the sizes of the nanodots. In comparison with e-beam lithography, the present method has the advantages of ease of control and relatively low cost.

2. Experimental

The experimental procedure is described as follows. A nickel film with a thickness of 10 nm was prepared by e-beam evaporation onto a silicon substrate with a 1- μ m silicon dioxide buffer layer. The nano-oxidation was

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performed in a commercial AFM (Smena-A, NT-MDT, Russia) with the use of silicon probes (NSC15, Micro-Masch, Russia) under ambient conditions. Negative voltage biases were applied to the probes with the sample grounded, and desired patterns were created by the AFM lithography software. After the oxidation, the sample was then dipped into a nitric acid solution to remove the unoxidized nickel. On the other hand, the created nickel oxide patterns were not affected by the wet etching. Detail of the nano-oxidation of nickel can be found in a previous publication [15].

The nickel oxide patterns were put in the reaction chamber with a vacuum of 5×10^{-3} Torr. Hydrogen was then introduced into the chamber and the substrate was heated to 660 °C. The reactor pressure was adjusted to 3 Torr, and the sample was pre-treated by plasma for 10 min for the reduction of nickel oxide. A mixture of methane and hydrogen (1:4) gas flow was then introduced, and an inductive rf power of 250 W and a substrate bias of -400 V were used during the 40 min growth period. After the CNT growth, the chamber was allowed to cool in hydrogen atmosphere before exposure to air. The growth detail can also be found elsewhere [16].

3. Results and discussion

With a tip bias of -8 V, a nickel oxide square with a size of $4 \times 4 \mu\text{m}^2$ was generated and the image after the wet etching is shown in Fig. 1a. To verify if the nickel 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 pattern [15]. A 4×4 nickel oxide nanodot array generated with the application of -9 V, 0.7 ms pulses is shown in Fig. 1b. The average height and diameter are around 8 and 50 nm, respectively, as determined from cross section analysis.

The diameters of the nanodots can be varied by controlling the magnitude and/or the duration of the applied voltage pulse. The nanodots obtained with the

use of a constant bias of -10 V and 6 durations (0.15–3 ms) are shown in Fig. 2a. The diameters are ranging from 50 to 100 nm, and the heights are from 2.7 to 26 nm. The oxidation kinetics can be described by the following equations [14]:

$$\frac{dh}{dt} = R \exp\left(\frac{-h}{h_0}\right), \quad (1)$$

$$h = h_0 \ln\left(\frac{R}{h_0}t + 1\right), \quad (2)$$

where h is the oxide height, t the pulse duration, h_0 the characteristic height, and R the maximum rate. The growth rate dh/dt is equal to the oxide height divided by the pulse duration, and Eq. (2) is a direct integration of Eq. (1). The relationships between the growth rate and the oxide height, and the oxide height and the pulse duration are plotted in Fig. 2b and c, respectively. The R and h_0 from the linear fitting in Fig. 2b are equal to 33.2 nm/ms and 19.7 nm, respectively. In comparison with the R and h_0 obtained in our previous study on 15 nm nickel films, which were 0.25 nm/ms and 17.4 nm [15], respectively, the present R is roughly 2 orders of magnitude higher and the h_0 is in good agreement. The dramatic difference is apparently caused by the use of thinner nickel films in the present experiment, but the detail would need further investigation.

The fabricated nickel oxide patterns were then used as catalytic templates for the selective growth of CNTs. Fig. 3a shows the scanning electron microscope (SEM) image of an oxide square before growth, and Fig. 3b and c are the corresponding images of the vertically aligned multiwalled CNTs in different magnifications. Furthermore, a 2×2 square array of CNTs is also produced and shown in Fig. 3d. As can be seen clearly, the CNTs are present only on the defined regions as expected. Therefore, patterned growth of vertically aligned

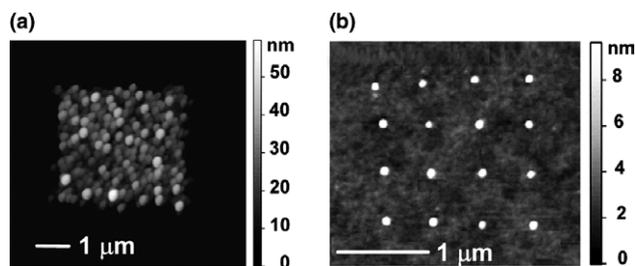


Fig. 1. AFM images of (a) a $4 \times 4 \mu\text{m}^2$ nickel oxide square created with a tip bias of -8 V, and (b) a 4×4 nickel oxide nanodot array created with the application of -9 V, 0.7 ms pulses.

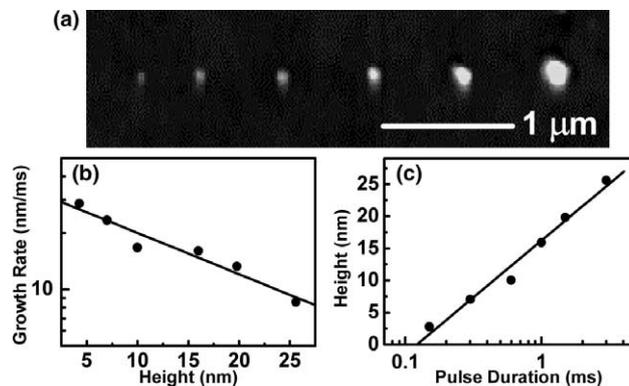


Fig. 2. (a) AFM image of nickel oxide nanodots created with -10 V pulses of various durations from 0.15 to 3 ms, and the corresponding plots of (b) growth rate versus dot height and (c) dot height versus pulse duration.

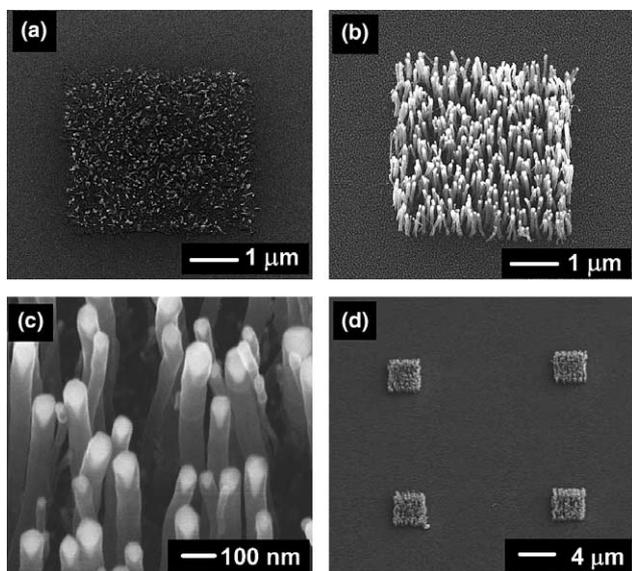


Fig. 3. SEM images of (a) an oxide square before growth, (b) and (c) the vertically aligned multiwalled CNTs selectively grown on the square in different magnifications, and (d) a 2×2 square array of CNTs.

CNTs can be achieved with ease by the present method. Judging from Fig. 3c, most of the CNTs have diameters in the range of 50–80 nm except for few small ones. In addition, the nickel catalysts appear at the tops and the tip growth mode is the preferred growth mode. The results are similar to our previous study using nickel films as catalysts [16], which indicates the nickel oxide can be used as effective as nickel at least for the present growth method.

As has been elaborated in the literature [4,9,10], preparation of catalysts with sizes of less than 100 nm is a prerequisite for the selective growth of single CNTs. Consequently, the oxide nanodots are valuable for the controllable growth of single CNTs. To find out the correlation between the dot size and the tube diameter, nanodots of various sizes were fabricated and the SEM image is shown in Fig. 4a. The average sizes are 81, 62, 47, 33, and 27 nm from top to bottom row, respectively. The grown CNTs are shown in Fig. 4b and the corresponding tube diameters are 57, 47, 40, and 27 nm. The growth was not successful on the smallest dots as can be seen, but it should be improvable after proper adjustment of growth parameters. The relationship between the tube diameter and the dot size is plotted in Fig. 4c. Since the tube diameter is roughly equal to the size of the catalyst as can be seen in Fig. 3c, the smaller tube diameter in comparison with the dot size in Fig. 4c can be reasonably attributed to the chemical reduction of nickel oxide to nickel before growth. It is also apparent that the tube diameter is strongly correlated with the dot size, which can be easily manipulated by adjustment of pulse duration.

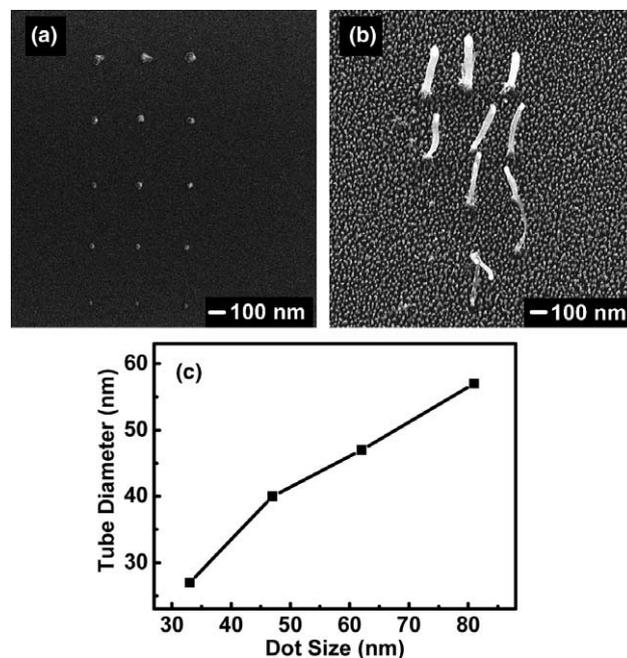


Fig. 4. SEM images of (a) nickel oxide nanodots of various sizes and (b) the vertically aligned single CNTs grown on the dots, and (c) the relationship between the tube diameter and the dot size.

4. Summary

To summarize, we have presented a novel method to achieve selective growth of CNTs based on AFM nano-oxidation. Vertically aligned CNTs have been successfully grown on the created nickel oxide catalytic templates by ICP-CVD. In addition, single CNTs have also been grown on isolated oxide nanodots and the tube diameter can be effectively controlled by the dot size. The present method has the major advantages of nanoscale resolution and relatively low cost in comparison with e-beam lithography, and is also potentially valuable for the construction of novel nanodevices employing CNTs with variable diameters and complex architecture.

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