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Growth mechanism and properties of the well-aligned-carbon-coated Si nanocones by MPCVD

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Abstract

In order to clarify the possibility to form Si nanocones under the same gas sources (CH_4 and H_2) and deposition system (microwave plasma chemical vapor deposition (MPCVD)), a process were successfully developed to synthesize the well-aligned amorphous carbon-coated Si nanocones (a:C-SNCs), and their growth mechanism is proposed. This process includes depositing 10 nm Co-catalyst on Si wafer by physical vapor deposition (PVD) and then followed by H-plasma pretreatment to form Co nanoparticles. The pretreated specimens were then used to synthesize various nanostructures under a higher negative substrate bias. The deposited nanostructures and their compositions were characterized by SEM, HRTEM, ED, EDS and Raman spectroscopy. The results indicate that the most important parameters for forming a:C-SNCs include a lower CH_4/H_2 ratio, a higher negative substrate bias and assistance of the carbon-soluble nano-sized catalysts, such as Co. Under a higher enough negative substrate bias ($\geq$240 V), the etching rates of the catalyst particles and the substrate by the positive species are greater than the carbon deposition rate; a:C-SNCs can be formed. We propose that the cone shape of the nanostructures is essentially resulted from a progressive reduction in catalyst particle sizes under the conditions of higher etching rate than deposition rate on the catalyst surfaces, which may be partially due to a reduction in the Co melting temperature by the presence of carbon in the Co matrix. This mechanism is supported by the facts that a:C-SNCs find no catalysts or very small catalysts on the tips; the catalyst sizes show no significant reduction in sizes after the same a:C-SNCs deposition conditions except no presence of carbon; the diameter of the cone base has no significant differences in size as the original catalyst size after H-plasma pretreatment. Our mechanism gives the guideline to form the nanocone structures by MPCVD with same gas sources (CH_4 and H_2).
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Keywords: Si nanocones (SNCs); Carbon nanotubes (CNTs); Microwave plasma chemical vapor deposition (MPCVD); Growth mechanism

1. Introduction

There is a considerable surge in research activity to find a superior material for field emitters for display, involving simplifying the process, longer life-time, higher emission efficiency and lower turn-on voltage [1,2]. To achieve these purposes, one of the important ways is to examine the relationships between the nanostructures and their properties, and to study their growth mechanisms. The past reports indicate that Si nanocones (SNCs) can be the candidate materials for field emission applications [3]; and some investigators suggested that SNCs can be used as the probe tips of atomic-resolution scanning tunneling microscopy (STM) and atomic force microscopy (AFM) [4–8]. There were many proposed methods to prepare the SNCs for these applications; e.g. using etching resist as the selective area technique to fabricate the SNCs pattern [9]. However, the progress in such sharp SNCs is hindered by its high work function, low electron conductivity, and poor stability [10]. In order to enhance its emission efficiency and stability, the additional process was added to protect the tip surface with a layer of diamond film [11], diamond-like carbon [12], or amorphous carbon [13]. In this work, we will propose a simple process to fabricate the well-aligned a:C-coated SNCs to minimize the processing steps.

It is well known that microwave plasma chemical vapor deposition (MPCVD) system with CH_4 and H_2 as source gases can be used to synthesized diamond film, diamond-

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like carbon (DLC), CNTs, Si–C–N nanotubes under presence of nitrogen, or carbon nanocones (CNCs), etc. [14–16]. There are many proposed mechanisms to explain the formations of various nanostructures, however, no mechanisms can be successfully conformed to our experimental results about formation of Si nanocones. In this article, we designed few simple experiments to fabricate the a:C-SNCs nanostructures with Co as catalyst by MPCVD and CH_4+H_2 as source gases, and to examine their growth mechanisms.

2. Experimental

The well-aligned a:C-SNCs on Si wafer were synthesized by MPCVD with CH_4 and H_2 as source gases and Co as catalyst. The process includes the following steps. First, the (100) Si wafers were coated with 10 nm Co by rf sputtering method and then followed by H-plasma pretreatment (100 sccm H_2, 400 W microwave power) for 10 min to obtain the well-distributed Co nanoparticles. The pretreated substrates were then deposited by MPCVD under various CH_4/H_2 ratios and substrate biases. Some as-deposited specimens were then post-treated under H-plasma atmosphere (100 sccm H_2, −320 V substrate bias, 800 W microwave power) to examine the possible reactions with the nanostructures. Table 1 shows the specimen designations and their deposition conditions. Furthermore, to examine effect of the presence of carbon or not in the catalyst particles on the bombarded nanostructures, there is one specimen which was H-plasma pretreated, carburized the catalyst nanoparticles in pure CH_4 plasma atmosphere (1 sccm CH_4, −320 V substrate bias, 800 W microwave power), and then followed by etching process under the post-treatment conditions (Sample A4 in Table 1).

Morphologies of the deposited nanostructures were characterized by thermal field emission SEM (FESEM; JSM-6500F), XTEM and high-resolution TEM (HRTEM; JSM-2010F). In which, the TEM specimens were prepared by emery paper grinding and followed by ion milling to reach few nanometers in thickness. The crystal structures, compositions and bonding structures of the deposited nanostructures were examined by electron diffraction (ED), energy dispersive spectroscopy (EDS) and Raman spectroscopy (HORIBA JOBIN YVON LABRAMHR).

Table 1
Specimen designations and their deposition conditions

Specimen designation[a,b]	CH_4/H_2 ratio (sccm/sccm)	Process time (min)	Post-treatment[c]	Remarks
A1	1/100	20	No	a:C-coated Si nanocones
A2	1/100	20	Yes	Si nanocones
A3	N/A	N/A	Yes	Si nano-columns
A4[d]	N/A	N/A	Yes	Si nanocones

[a] H-plasma pretreatment conditions: substrate=10 nm thickness Co coated Si, microwave power=400 W, bias=0 V, H_2=100 sccm.
[b] Other deposition conditions: base pressure=5 mTorr, working pressure=9 Torr, bias=−320 V, microwave power=800 W.
[c] H-plasma post-treatment conditions: H_2=100 sccm, bias=−320 V, microwave power=800 W, process time=20 min.
[d] Catalyst carburization pre-treatment conditions: CH_4=1 sccm, bias=−320 V, microwave power=800 W, process time=4 min.

3. Results and discussion

3.1. SEM morphologies and TEM images

Under the condition of CH_4/H_2 ratio of 1/100 sccm/sccm, the diamond films could be grown by MPCVD on Si wafer without catalysts, as reported in the literature [17]. However, with the assistance of the Co nanoparticles, the well-aligned cone-shaped nanostructures instead of diamond micro-crystals could be synthesized under the same gas ratio, as depicted in Fig. 1. It was synthesized under a substrate bias of −320 V (Sample A1). It demonstrates a cone number density around 302 Gcones/inch^2, i.e. one cone occupies about 46^2 nm^2. It is interesting to note that CNTs or diamond micro-crystals were not found under such a high substrate bias. The observations may imply that the carbon deposition rate on the catalyst surfaces is less than the removal rate due to large bombardment effect under the great substrate bias.

To examine the structures of these cone-shaped nanostructures, the corresponding XTEM microstructures and HRTEM lattice image of Fig. 1 are shown in Fig. 2(a) and (b), respectively. The inset of Fig. 2(b) is the ED pattern of the inner of the cones, signifying a crystalline Si lattice. Fig. 2(a) indicates that the nanostructures are essentially covered with a layer of amorphous carbon, as identified by EDX analyses. In other words, the nanostructures are basically the amorphous carbon-coated Si nanocones (a:C-SNCs). This demonstrates one main advantage of our process that it requires no additional process to coat the amorphous carbon to enhance the emission efficiency of Si cones, as proposed in the literature [13].

To compare morphologies of the Si nanostructures under the pure and the pre-carburized Co-catalysts, we conduct the same deposition process except under pure H-plasma atmospheres, respectively. Figs. 3 and 4 show the corresponding SEM morphologies being the column-shaped and cone-shaped Si nanostructures, respectively (Samples A3 and A4). It is noted that the Co nanoparticles are on the tips of both Si nanostructures, but the sizes of the catalyst nanoparticles of Sample A3 are five times larger than the catalysts of Sample A4 (about 100 nm versus 20 nm). By comparing the process conditions for Figs. 3 and 1 (Samples A3 and A1, respectively.), it is interesting to find that the morphologies of the Si nanostructures were changed from column-shape to cone-shape by adding CH_4 into H_2 plasma atmospheres. In other words, presence of carbon in the pre-carburized catalysts or in the processing plasma atmosphere

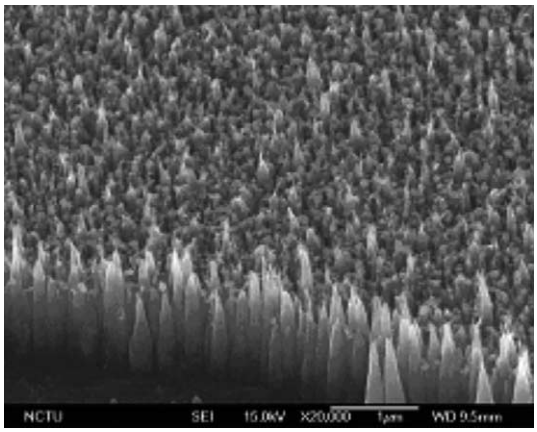

Fig. 1. SEM image of the as-deposited a:C-SNCs (Sample A1) with 20 min deposition time.

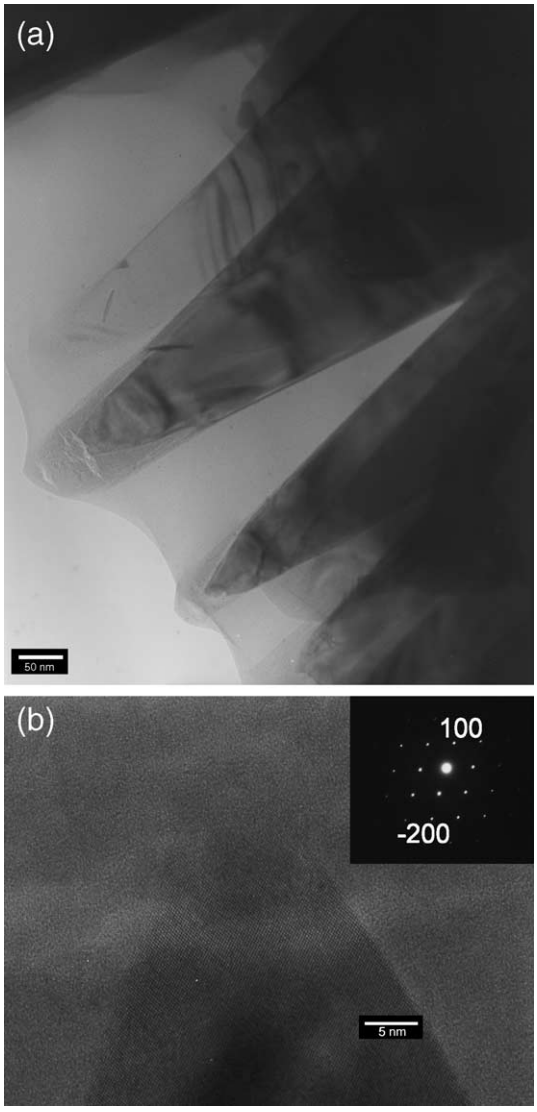

Fig. 2. (a) XTEM lengthwise cross-section nanostructures, and (b) HRTEM lattice image and ED pattern (inset) of the as-deposited a:C-SNCs (Sample A1).

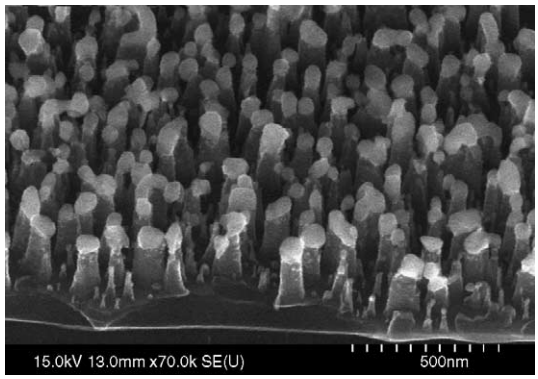

Fig. 3. SEM image of the as-deposited nanostructures under the post-treatment of 20 min on the Co-coated Si substrates (Sample A3).

can greatly enhance the formation of the cone-shaped nanostructures. The possible growth mechanisms to form different morphologies of the Si nanostructures are an important issue and will be discussed in the next paragraphs.

3.2. Raman spectra of the nanostructures

The as-deposited and post-treated a:C-SNCs were analyzed by Raman spectroscopy to examine the possible reaction products in the nanostructures. The results indicate that Raman spectra for the as-deposited a:C-SNCs (Sample A1) are similar to that for diamond-like carbon, signifying existence of amorphous carbon layers on tops of the nanostructures, which are verified in the previous paragraph. In contrast, the typical Raman spectrum for the post-treated a:C-SNCs is shown in Fig. 5 (Sample A2), where an additional Raman peak around 1430 cm^{-1} can be found. This may be due to the fact that the amorphous carbon layer of the nanostructures is partially removed after H-plasma post-treatment; therefore, the surfaces of the embedded Si nanocones can be penetrated by laser beam to detect the existence of very thin SiC layer on the surfaces of Si nanostructures. In addition, the cone-shaped morphologies of the as-deposited nanocones are not significantly changed

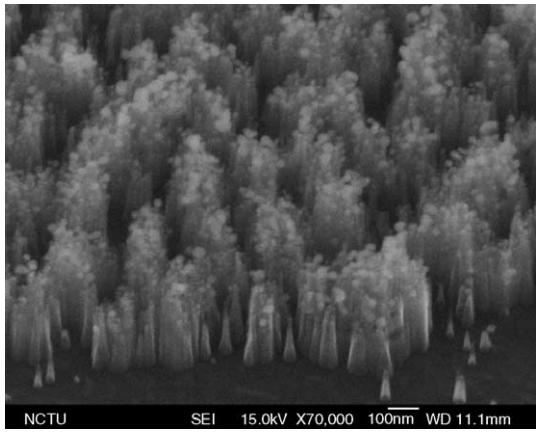

Fig. 4. SEM image as indicated in Fig. 3, except the Co nanoparticles were conducted a carburization pretreatment (Sample A4).

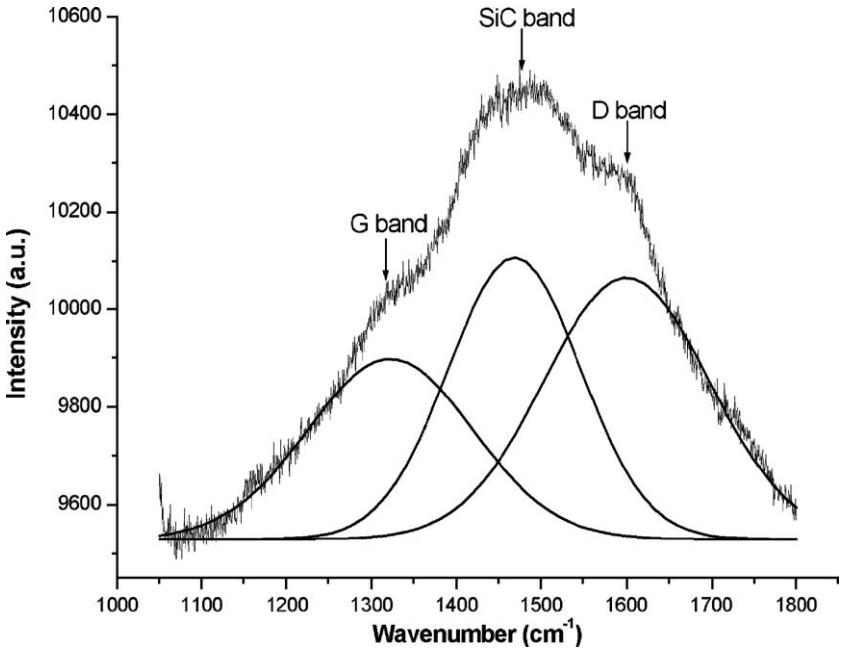

Fig. 5. Raman spectrum of the post-treated a:C-SNCs (Sample A2).

after H-plasma post-treatment, indicating a higher resistance of SiC layers on nanocones to plasma attack.

3.3. Mechanism of amorphous carbon-coated Si nanocones deposition

To explain the possible mechanisms of forming a:C-SNCs, we propose a lithography-like process. From the experimental results, it seems to indicate that the required conditions to form Si nanocones are assistance of the catalysts, a higher negative substrate bias, and existence of low carbon concentration in the atmosphere or in the catalyst particles. By adding CH_4 in the atmosphere or the pre-carburized catalyst particles, it is essential to let the catalyst particles to form Co–C solid solution, which may greatly decrease the melting point of the nanoparticles. Effect of a higher substrate bias is basically to accelerate the bombarding rates of the positive species to gradually dissociate the nanoparticles to become smaller in sizes. In other words, under a greater substrate bias, the bombarding effect may inhibit the CNTs growth and enhance the etching effect on the Si wafers. The progressive decrease in sizes and their masking effects of the catalyst particles during process period may be responsible for the cone-shape formation. Therefore, the diameters of the cones at the cone bases are almost the same sizes as the nanoparticles at the beginning of the process due to their masking effects. This can also be used to explain why the cone sizes are not sensitive to the processing time. Our mechanism is also in agreement with the facts that a higher substrate bias and a decrease in melting points due to presence of carbon in the catalysts are two favor conditions to accelerate the dissociation rate of the nanoparticles. Without the presence of carbon in the catalyst, there are no significant decreases in particle sizes during process period; therefore, the column-shaped Si nanostructures will result (Sample A3).

4. Conclusions

In this work, we successfully developed a simple MPCVD process to minimize the processing steps to fabricate the well-aligned a:C-SNCs on Si wafer with CH_4 and H_2 as source gases. The results show that the favor conditions to form a:C-SNCs include (1) a higher enough negative substrate bias (>-240 V), and (2) presence of carbon in catalysts or in the reaction atmosphere, i.e. the assistance of the catalysts is required. In terms of growth mechanism of the Si nanostructures, the favor formation conditions suggest that the progressive decrease in sizes and their masking effects of the catalyst particles during process period may be responsible for the formation of a:C-SNCs. The function of a strong substrate bias is basically to enhance the bombardment effect to the substrate and to inhibit the carbon diffusion in the catalyst or along its surface for forming CNTs. The function of carbon is essentially to accelerate the sputtering rate of the catalyst particles by reducing the melting temperature. This is in agreement with the fact that the nanostructures will become the column-shaped Si rods with no presence of carbon.

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