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Carbon nanotubes grown using cobalt silicide as catalyst and hydrogen pretreatment

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Abstract

Cobalt catalytic-layers 25 nm were deposited by sputtering on silicon substrates. At the pretreatments, hydrogen plasma was conducted for 4–16 min at 600 °C in a MPCVD system. Pretreated samples were characterized using SEM and AFM. Surface morphologies of catalytic-layers were changed after hydrogen plasma pretreatments. The cobalt layers became discontinuous and some nanoparticles were formed. With pretreatments for a long time, nanoparticles tended to agglomerate to reduce surface energy and larger nanoparticles were observed. It is believed that the optimum pretreatment condition for the growth of carbon nanotubes could be achieved because relatively high growth failure and nanofibers (>100 nm) was observed for shorter and longer than 12 min pretreatment, respectively. It is found that the hydrogen pretreatment is a crucial step for the making of nucleation sites in the synthesis of carbon nanotubes using cobalt silicide as catalyst on Si substrates. After the pretreatment, mixture gases of hydrogen and methane were then flowed into the chamber for 12 min, samples were characterized using SEM, TEM and Raman spectrum. Carbon atoms were adsorbed on the islands of catalysts, and then diffused into the edge of nanotubes. Cobalt silicides were formed due to high processing temperature, and cobalt atoms tended to diffuse and stay on the silicon substrates, which enhance carbon nanotubes to grow under the root growth mechanism.

Keywords: Microwave CVD; Cobalt silicide; Root growth mechanism

1. Introduction

Since Iijima's discovery of carbon nanotubes in 1991 [1], nanometer-scale tubular forms have been the subjects of intensive research due to

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their unique properties [2]. The nano-size effects show unique size distribution and hollow geometry, which result in unique electrical, mechanical, and chemical properties and wide potential applications. In fact, carbon nanotubes have shown considerably complex properties of microstructure depending on preparation and pretreatment.

Various methods, such as arc discharge, laser ablation, chemical vapor deposition (CVD), and template-directed synthesis, have been used for the growth of carbon nanotubes in the presence of catalyst particles [3–6]. Among them, CVD technique is the simplest and lowest-cost method, and can be operated at relatively low temperatures, especially with plasma enhancement [7].

In the CVD process, properties of the catalyst and pretreatment control are very important because they will affect growth and resulting properties of carbon nanotubes. Understanding of pretreatment would enable us to design and control properties of the carbon nanotubes [8,9]. In this work, we study the properties of cobalt silicide catalysts pre-treated by hydrogen plasma and deposition of carbon nanotubes in a MPCVD system. The effects of hydrogen plasma pretreatment were discussed.

2. Experimental procedures

2.1. Preparation of catalysts

The substrates used in experiments were 6-in. p-type (1 0 0) orientated silicon wafers with resistivity of 15–25 Ω cm. In order to remove chemical impurities and particles, the wafers were cleaned by standard RCA cleaning procedures. Twenty five nanometer cobalt films were deposited with a power of 700 W and a sputtering pressure of 6.4 mTorr (0.85 Pa).

2.2. Pretreatment and synthesis of carbon nanotubes

A 915 MHz microwave plasma chemical vapor deposition (MPCVD) system was used for pretreatment and synthesis of carbon nanotubes. The applied microwave power was 700 W and base pressure of the system was below 2×10^{-3} Torr. Cobalt films were heated via a graphite heater at 600 °C and pretreated by hydrogen plasma for 4, 8, 12, and 16 min, respectively. The surface of cobalt catalysts were examined using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The catalyst films were observed by transmission electron microscopy (TEM). To grow carbon nanotubes, hydrogen (150 sccm) and methane (50 sccm) were introduced into the chamber at 600 °C for 12 min after pretreatments with various periods. The resulting carbon nanotubes were examined by SEM, TEM, and Raman spectroscopy.

3. Results and discussion

3.1. Effects of hydrogen plasma pretreatment

Fig. 1 shows SEM images of Co/Si system after pre-treatments at 600 °C for various periods. The cobalt layers gradually became discrete island structure with increasing pretreatment time, as shown in Fig. 1. Cobalt atoms tended to diffuse on the surface of silicon substrate during hydrogen plasma pretreatment, and some discontinuous nanoparticles were formed after hydrogen plasma pretreatment. Moreover, nanoparticles tended to agglomerate to reduce surface energy and larger nanoparticles were found for a long pretreatment time, as indicated in Fig. 1. In fact, only high-temperature thermal treatment would result in slight agglomeration effect on the catalytic-layers, as shown in Fig. 2. It is believed that diffusion, nucleation and etching would occur during hydrogen plasma pretreatment. The combined effects contribute to formation of nanoparticles with small spacing. These can act as the nucleation sites for growth of carbon nanotubes.

Fig. 3 shows AFM images of Co/Si systems after hydrogen plasma pretreatments for various time. It is observed that sizes of cobalt silicide nanoparticles were initially decreased with increasing pretreatment time. Uniform catalytic-particles were formed on the substrate after the pretreatment for 12 min. The nuclei seem not to agglomerate with each other. The hydrogen plasma pretreatment also provides cleaning effect which will help

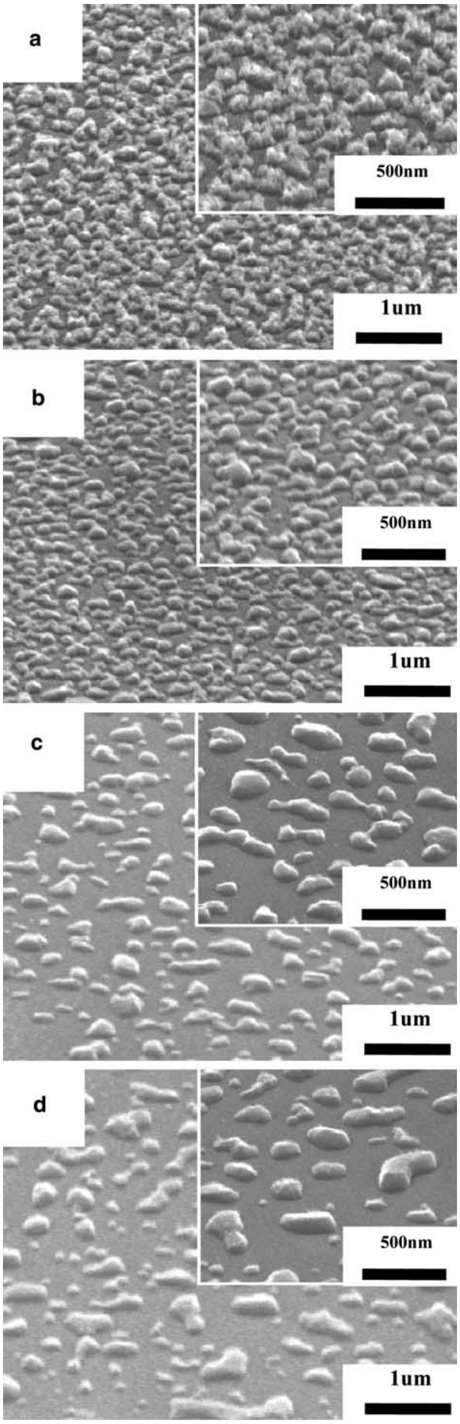

Fig. 1. SEM images of Co/Si system after pre-treatment at 600 °C for (a) 4, (b) 8, (c) 12, and (d) 16 min.

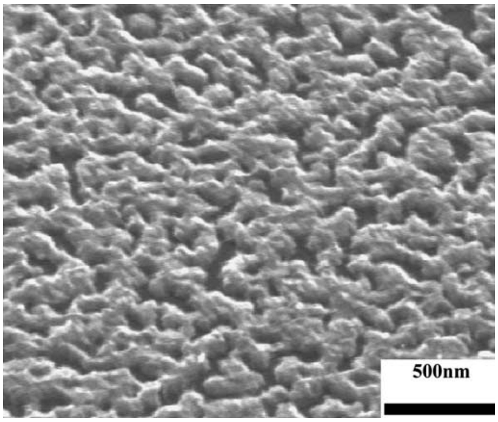

Fig. 2. SEM image of the Co/Si system after only thermal treatment at 600 °C.

growth of carbon nanotubes. The RMS surface roughness of the catalytic-layer changed from 22.35 to 5.13 nm as pretreatment time increased from 4 to 16 min, as shown in Fig. 4.

Detailed schematic illustrations of the microstructures of cobalt catalytic layers after different pretreatments are displayed in Fig. 5. At the pretreatment for 4 min, some discrete cobalt catalytic nanoparticles were formed, as shown in Fig. 5(a). With longer pretreatments (8 min), etching effect resulted decrease and increase of the size and number of particles, respectively as shown in Fig. 5(b). As the pretreatment time increase to 12 min, uniform catalytic nanoparticles with proper spacing were formed on the silicon substrate as shown in Fig. 5(c). This distribution of catalytic nanoparticles would provide good nucleation sites for growth of carbon nanotubes. With further increasing pretreatment time, catalytic nanoparticles tended to agglomerate and hence could not provide uniform nanoparticles for the growth of carbon nanotubes, as shown in Fig. 5(d).

It is indicated that hydrogen plasma pretreatment is a crucial step for nucleation sites in synthesis of carbon nanotubes using cobalt silicide as catalyst on silicon substrates.

3.2. Growth and properties of carbon nanotubes

Mixture gases of hydrogen (150 sccm) and methane (50 sccm) were flowed into the chamber

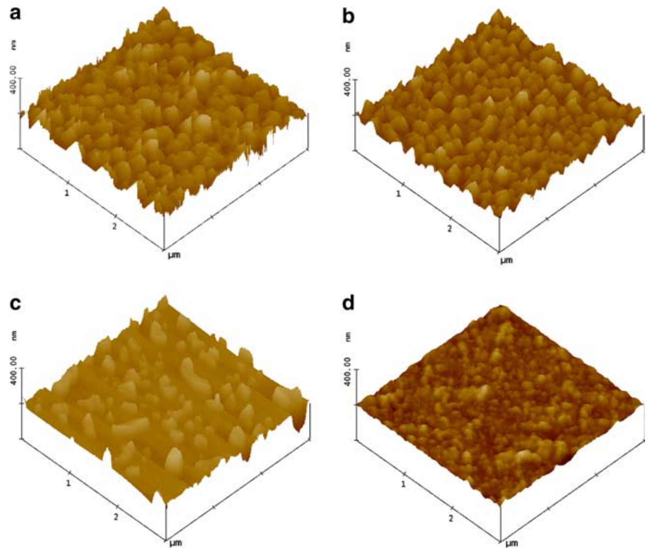

Fig. 3. AFM images of Co/Si systems after pre-treatments at 600 °C for (a) 4, (b) 8, (c) 12, and (d) 16 min.

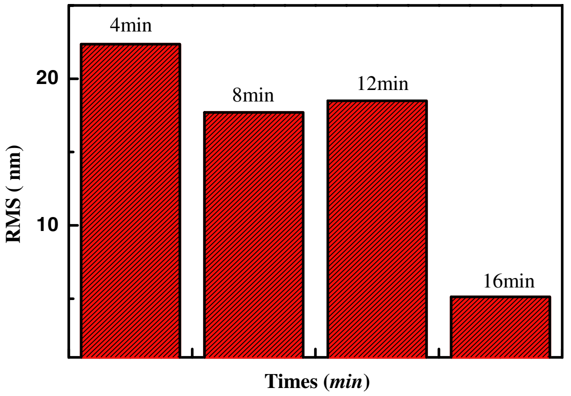

Fig. 4. RMS roughness as a function of plasma pre-treatment time.

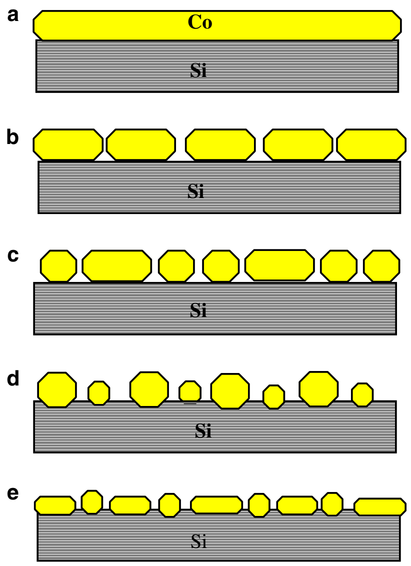

Fig. 5. Schematic illustrations of the microstructures of cobalt catalytic layers after pretreatments for (a) 4, (b) 8, (c) 12, and (d) 16 min.

at 600 °C for 12 minutes after pretreatments. Carbon atoms would first adsorb on islands of catalysts during growth, and then adsorbed carbon atoms could diffuse to the edge of nanotubes. The SEM image of resulting carbon nanotubes for different pretreatment are shown in Figs. 6(a)–(d).

Relatively, high growth failure and low yield carbon nanotubes are clearly shown in Figs. 6(a) and 6(b). Fig. 6(c) shows that the 12 min pretreatment could provide better growth of carbon nanotubes. Moreover, for the longer pretreatment time, several nanofibers (>100 nm), can be observed in Fig. 6(d). It is believed that the optimum pretreatment condition for the growth of carbon nanotubes could be achieved because

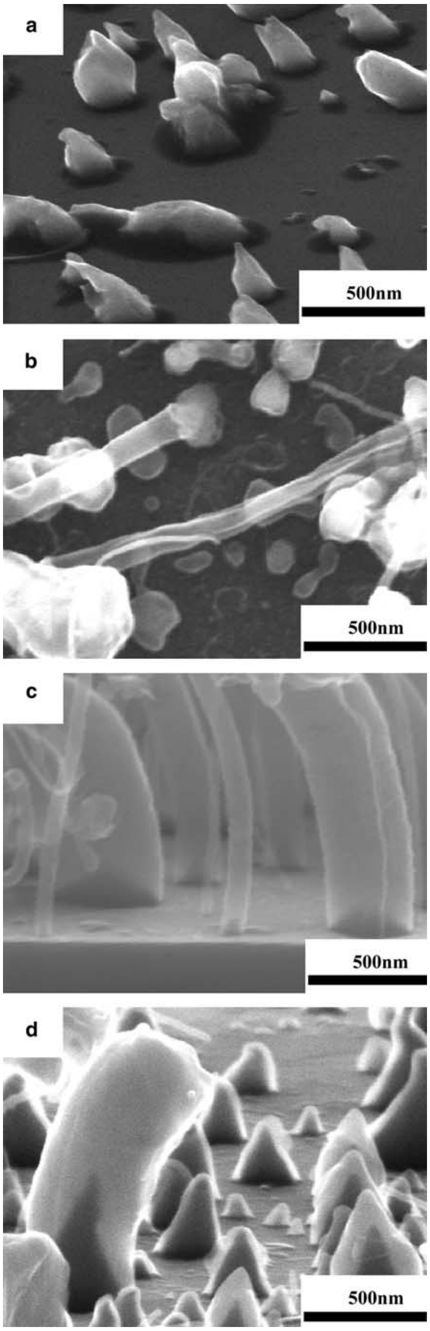

Fig. 6. Various pretreatment time(a) 4, (b) 8, (c) 12, and (d) 16 min and growth 12 min, respectively.

relatively high growth failure and nanofibers was observed for shorter and longer than 12 min pretreatment, respectively.

Raman spectrum of carbon nanotubes exhibits mainly two bands at 1328 cm^{-1} (D-band) and 1593 cm^{-1} (G-band). The signal of D-band is attribute to disorder-induced features due to the particle size effect, lattice distortion, or amorphous carbon background signals. The G-band is resulted from the stretching vibration mode of graphite crystals. For the sample, I_g is higher than I_d, as shown in Fig. 7, indicating relatively low

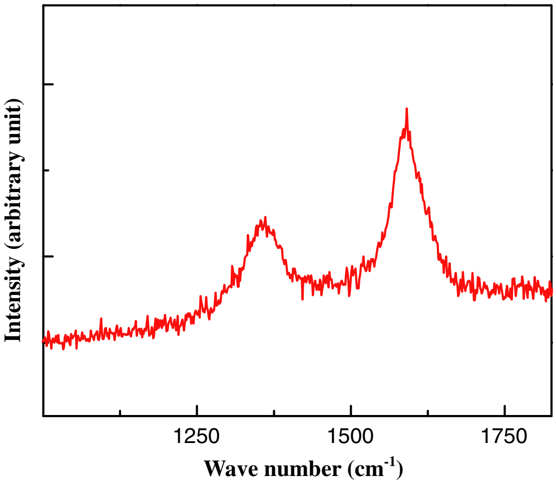

Fig. 7. Raman spectrum of carbon nanotubes growth for 12 min and pretreatments.

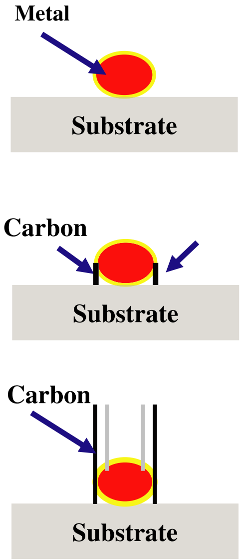

Fig. 8. Root growth mechanism of the carbon nanotube.

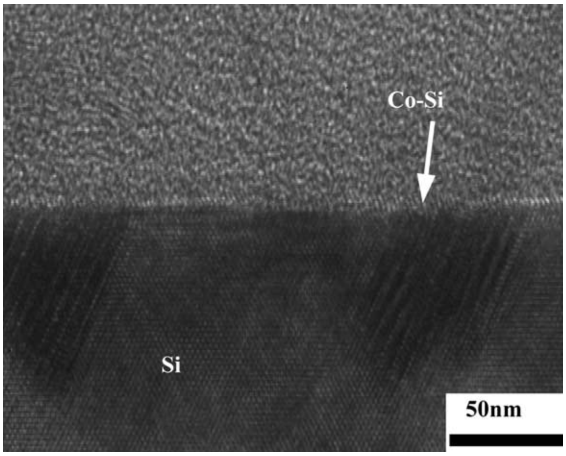

Fig. 9. Cross-sectional TEM image of carbon nanotube/$CoSi_x$/Si system.

disordered carbon structures. Growth of carbon nanotubes on the surface of metallic cobalt is due to the phase transformations in nano-sized systems. Many factors affect this process. It was deduced from the microscopic observations of catalysts. From microstructural analyses of as-grown carbon nanotubes, root growth mechanism is found for carbon nanotubes grown using cobalt silicide as catalyst and hydrogen pretreatment.

Fig. 8 shows schematically root growth mechanism of carbon nanotubes. Cobalt tended to diffuse and stay on the silicon substrate for carbon nanotube/$CoSi_x$/Si system, as shown in the cross sectional TEM image of Fig. 9. Carbon atoms were adsorbed on the islands of catalysts, and then diffused to the edge of nanotubes. Cobalt silicide enhances carbon nanotubes to grow under the root growth mechanism and the grown carbon nanotubes have a multi-wall structure as shown in Fig. 10.

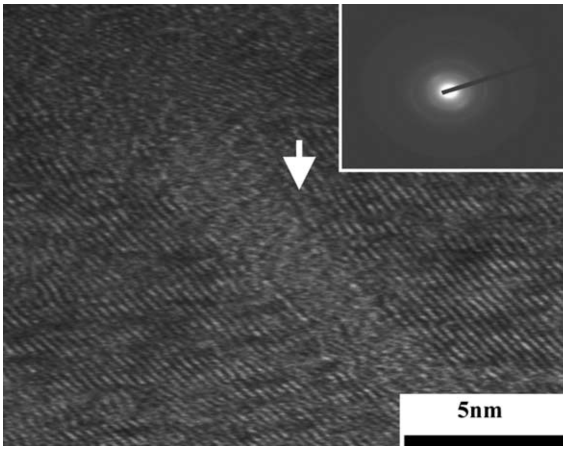

Fig. 10. Cross-sectional TEM image of the multi-wall carbon nanotube.

4. Conclusions

Cobalt films were used as catalysts for growth of carbon nanotubes. Cobalt catalytic-layers were pretreated by hydrogen plasma at 600 °C, which enhanced growth of carbon nanotubes. Hydrogen plasma pretreatment results in discontinuity of the film and the catalysts show island structure after pretreatments. It is found that hydrogen plasma pretreatment had resulted in etching, cleaning, and agglomeration on the catalytic-layers. Only thermal treatment would result in slight agglomeration effect on the catalytic-layers. It indicates that hydrogen plasma is a crucial step for growth of carbon nanotubes using cobalt or cobalt silicide as catalyst. Cobalt silicides were formed due to high processing temperature, cobalt tended to diffuse on silicon substrates during pretreatment. Root growth mechanism is found for carbon nanotubes grown using cobalt silicide as catalyst and hydrogen pretreatment.

Acknowledgments

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