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Controlled growth of Fe catalyst film for synthesis of vertically aligned carbon nanotubes by glancing angle deposition

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Abstract

Ultra-thin (5 nm) Fe catalyst films were deposited by a metal vapor vacuum arc (MEVVA) ion deposition system. The surface morphologies of the films were controlled by varying the angular relation of the substrate surface with respect to the incoming vapor direction. The Fe films grown with the incident flux at an angle of 30° with respect to the surface were shown to be smooth and after thermal treatment in NH_3 the particles with a narrow size distribution and high N/Fe atom ratio were followed. When they were used to synthesize carbon nanotube arrays, pure and well-aligned multi-walled carbon nanotubes were obtained.

Keywords: Fe film; Deposition angle; Carbon nanotubes

1. Introduction

Since the discovery of carbon nanotubes [1], they have attracted considerable interest due to their electrical, optical and mechanical properties and attractive potential applications [2–4]. Many researches have been reported on the synthesis of carbon nanotubes [5–8]. However, the mechanisms of carbon nanotubes (CNTs) growth and their orientation are not well understood. Still much work should be done to optimize the growing processes. For the moment, the main synthesis methods include the arc-discharge [5], laser-ablation [6] and chemical vapor deposition (CVD) methods [7,8]. Among different methods, the CVD has been used widely, as it provides a way for large area synthesis of vertically aligned carbon nanotubes for electron emitters [9]. Moreover, this process makes it possible to control the size and growth density of CNTs by dispersing the catalyst on substrates and adjusting the reaction parameters [10,11]. In many cases, the catalyst is deposited initially in the form of a thin film by sputtering or thermal evaporation, followed by high temperature processing in gases like hydrogen, nitrogen or NH_3 to form small nano-particles [10,11]. The dimensions of the catalyst particles determine the diameter and structure of nanotubes grown in a CVD process. In turn, these dimensions depend on many parameters such as the film thickness, the temperature and duration of the thermal processing, and so on. However, the process of the nano-particles formation from the deposited catalyst film is still poorly characterized.

The influence of deposition angle on the microstructure of thin film has been reported by a several research groups [12–15]. Liu et al. [13] reported that when the incident flux is perpendicular to the substrate, Fe films with a closely packed microstructure were observed. For oblique incidence, deposited Fe films showed columnar morphology. The columns are inclined from the substrate normal toward the vapor incidence direction. They believed that thin films develop columnar morphologies generally under low adatom mobility conditions, thus column formation is due to a self-shadowing mechanism [14]. In other words, during the growth of obliquely deposited films, the highest features of the film will geometrically shadow other surfaces of the film from direct impingement by the incoming vapour flux. However, they haven't discussed the effect of oblique incidence of vapor beam flux on the surface

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morphologies of Fe films and the initial nucleation phase and the initial layer.

In this work, the deposition angle, which is the angle subtended by the incoming flux and the substrate surface, has been shown to be an important role for the surface morphologies of 5 nm thick Fe films and hence the formation of nano-sized catalyst particles in NH_3 at reaction temperature. This determined the morphologies of aligned carbon nanotubes synthesized.

2. Experimental section

Thin iron films (5 nm thickness) were deposited on n-type (111) Si wafers with resistivity 4–4.8 Ω cm by a metal vapor vacuum arc (MEVVA) ion deposition system at room temperature. Fig. 1 shows the schematic diagram of the apparatus. Fe stick serving as the cathode is used for Fe source. Fe plasma is generated by the arc between the cathode and anode and fluxed into the chamber through plasma duct in which large particles were filtered. The remaining Fe ions were attracted by the bias (100 V) of the silicon wafer and deposited on the surface. During the deposition, Fe ion beam flux was fixed at 4 mA. Before deposition, the chamber was vacuumed to 10^{-3} Pa through a vapor pump and the sample bombarded by Fe ions at 3000 V negative bias to clean the surface and enhance the adherence of Fe film to Si substrates.

The synthesis of aligned carbon nanotubes was conducted in a horizontal thermal chemical vapor deposition (TCVD) system by decomposition of C_2H_2. The as-prepared Fe/Si catalyst was placed in the reaction region of the horizontal quartz-glass tube (inner diameter 110 mm and length 1200 mm). The reaction region was then heated up to 580 °C in H_2 and Fe catalyst deoxidized for 60 min. After that, the reaction region was continuously heated up to reaction temperature in hydrogen. Prior to deposition reaction, the Fe catalyst was pretreated for 10 min in NH_3 with a flow rate 200 ml/min. Subsequently, NH_3 was removed by H_2 in-flow rate 400 ml/min. The mixing gas C_2H_2 and H_2 with a ratio 90/600 ml/min was introduced into the reaction region and the reaction proceeded for 30 min. The samples were cooled in N_2 and observed using filed emission scanning electron microscope (FESEM). During the deposition of Fe films, the angle of incidence was varied to study its influence on the morphologies of the films and then the aligned carbon nanotubes synthesized. Atomic force microscope (AFM) was used to observe the surface topologies of Fe films before thermal treatment.

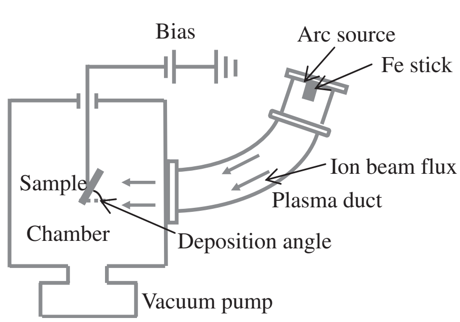

Fig. 1. Schematic diagram of the metal vapor vacuum arc (MEVVA) ion deposition system.

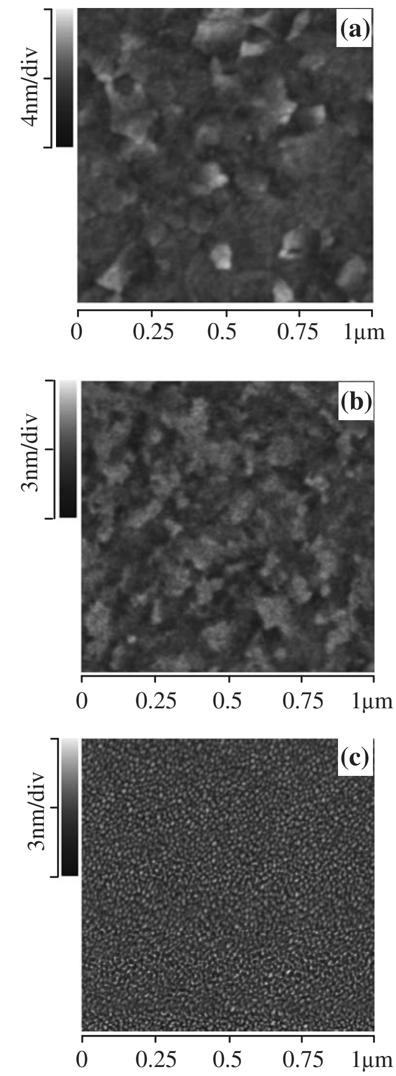

Fig. 2. AFM morphologies of Fe films deposited at 90° (a), 60° (b) and 30° (c) of deposition angles.

3. Results and discussion

The deposition angle was shown to affect the surface morphologies of the films greatly during the deposition process. Fig. 2 showed the AFM images of the surface topography of Fe films on Si wafers deposited with different angles of incidence. It is clearly seen that the surface features of Fe films become smoother as the angles of incidence decreased. For normal incidence, many salient features can be seen (as shown in Fig. 2a). With decreasing the deposition angle to 60°, the salient features spread and the heights decreased, so that the films become smoother (as shown in Fig. 2b). When the angle of incidence further decreased to 30°, the salient features almost disappeared and the Fe films on silicon wafers become most flat.

Results of thermal treatment are also different for the films deposited under different deposition angles. Fig. 3 shows the FESEM images and the corresponding histograms of the Fe