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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.

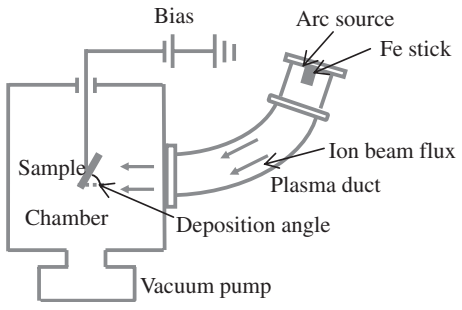

Fig. 1. Schematic diagram of the metal vapor vacuum arc (MEVVA) ion deposition system.

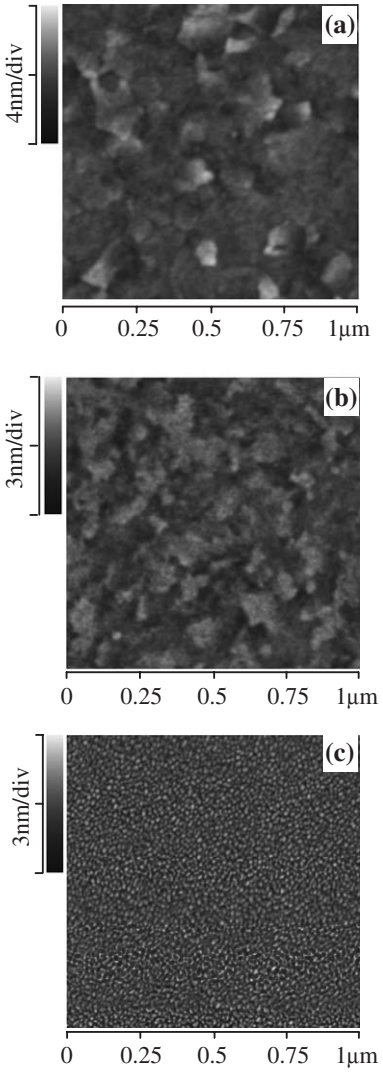

Fig. 2. AFM morphologies of Fe films deposited at 90° (a), 60° (b) and 30° (c) of deposition angles.

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

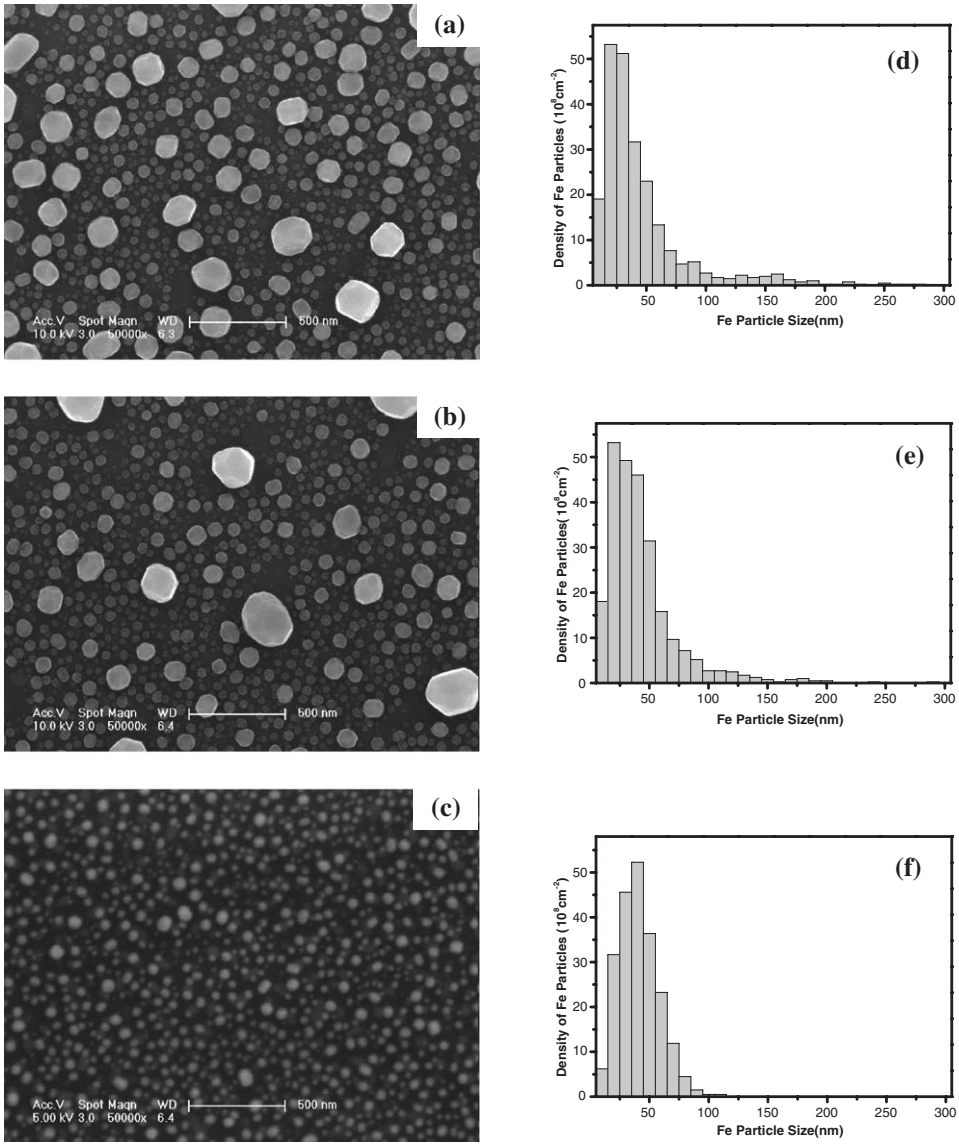

Fig. 3. SEM morphologies of 5 nm Fe films produced under different deposition angles after pretreated in NH_3 for 10 min and corresponding size histogram of Fe particles: (a),(d) 90°; (b),(e) 60°; (c),(f) 30°.

catalyst particles resulted from Fe films after pretreatment for 10 min in NH_3. From Fig. 3, the size distribution of Fe catalyst particles formed was varied greatly with different deposition angles. Fig. 3a indicates that the formation of catalyst particles or grains with relatively high size variation can be observed after pretreatment of Fe film deposited with normal incidence. As the deposition angle decreased to 60°, the number of the large particles formed in the thermal treatment decreased greatly (Fig. 3b). When the deposition angle further decreased to 30°, the catalyst particles are more uniformly distributed over the surface of the substrates (as shown in Fig. 3c).

For the precise analysis of the uniformity of catalyst distribution along the substrate (silicon) surface, it is helpful to compare the histograms of catalyst particles distribution (as shown in Fig. 3d, e and f). For normal incidence, the diameters of the particles range from several nanometers to about 280 nm, but most of them concentrated around 20 nm. However, the density of the large particles centered at 150 nm is also high, which leads to a bimodal distribution of Fe particle size. With decreasing the deposition angle to 60°, the range of the particle size decreased being in the range of 0~200 nm. The relative density of 40~50 nm particles increased greatly and that of about 150 nm of particles decreased rapidly. With the deposition angle further decreased to 30°, the particle size was less than 100 nm and centered at about 40 nm.

The above Fe catalyst deposited with different deposition angles were used to synthesize multi-walled carbon nanotube arrays during the same process. Fig. 4 shows the FESEM images of the corresponding multi-walled carbon nanotube arrays. From Fig. 4, the density of carbon nanotubes increased from 96 to 172 μm^{-2} and the carbon nanotube arrays showed better alignment as the deposition angle decreased from 90° to 30°. Carbon particles in the arrays also decreased with a decrease in the deposition angle and pure carbon nanotube

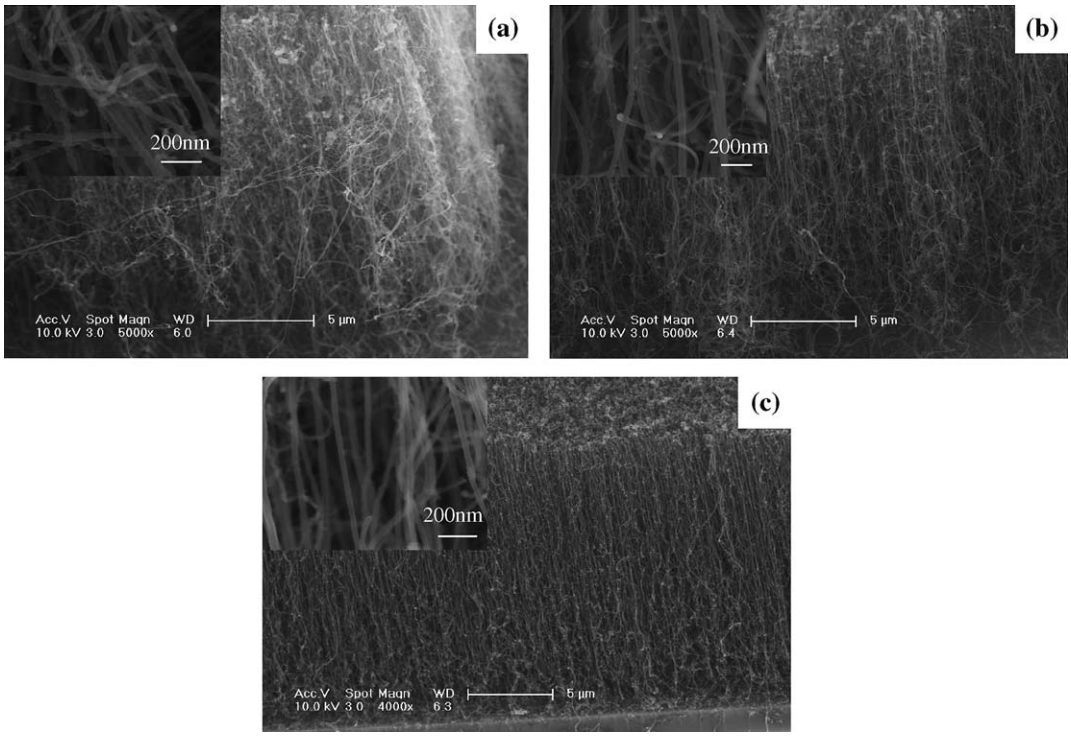

Fig. 4. SEM morphologies of carbon nanotube arrays fabricated using Fe/Si catalyst deposited under different deposition angles: (a) 90°; (b) 60°; (c) 30°. The inset images are the close view of the side of the arrays.

arrays were obtained for 30° of deposition angle. From the inset images, the diameters of the tubes varied considerably (from several nanometers to about 90 nm) for 90° deposition angle and became relatively more uniform as the deposition angles decreased to 60°. When the glancing deposition angle further decreased to 30°, carbon nanotubes with most uniform diameters centered at about 40 nm were synthesized (as shown in Fig. 4c). In addition, statistical analysis showed that no carbon nanotubes with the diameter of more than 90 nm were obtained, indicating the critical size of catalyst particles for the growth of carbon nanotubes should be about 90 nm in our experiment.

Thin film growth is a complicated process, especially for early stage of growth [16]. The growth of thin films will start with a random distribution of nuclei which will act as locations for further growth. If an atom arriving at the substrate encounters a nucleus, it will travel along its contour and get trapped at some point [15]. With the Fe ions continue arriving at the surface of the substrate, the as-formed nuclei will grow and form islands. According to Lennard-Jones' calculation [17], an atom which arrives perpendicular to the film surface will loose its excess energy in a few nanoseconds and travel only a few atomic distances during the period of accommodation. When the adatoms arrive the top of the islands, they will stay and tend to the formation of salient features on the film surface.

The situation could be different for an atom arriving obliquely at the film surface. To become an adatom it only needs to loose its component of kinetic energy perpendicular to the film surface, but it can keep its parallel component. This has been called conservation of parallel momentum [18]. Due to conservation of parallel momentum, the adatoms will continue travelling in the direction given by the project of the vapour beam direction. So the possibility exists that obliquely arriving atoms will travel much faster and scatter more than in the case of perpendicular incidence. It is visible that the parallel momentum will increase and the adatoms show increasing directional diffusion when the deposition angle is decreased. When the adatoms deposited on the top of an island can migrate to the edge, the film growth proceeds by a layer-by-layer mode [19]. Therefore, the surface became more and more smooth with the decrease of deposition angle.

The surface morphologies that affected the size distribution of Fe particles formed after heat treatment. The above results indicated that the salient features of the films should be responsible for the formation of the large particles due to the sintering of crystallite grains during the thermal pretreatment. Therefore, for 90° incident angles, the large variation of the catalyst nano-particle sizes were formed on the substrates due to the large number of salient features. With the deposition angle decreased to 60° the salient features on the surface of Fe films were decreased and hence the corresponding number of the large Fe catalyst particles decreased after thermal treatment. As the deposition angle further decreased to 30°, Fe catalyst particles with a narrow size distribution were obtained and few large particles were seen due to the disappearance of salient features on the surfaces of Fe films.

As we know, catalysts played a critical role in the synthesis of carbon nanotubes. Their densities and sizes controlled the morphologies of CNT arrays [20]. Therefore, for higher deposition angle (90° and 60°), the large variation of the diameters of the CNTs can be attributed to the large variation of the sizes

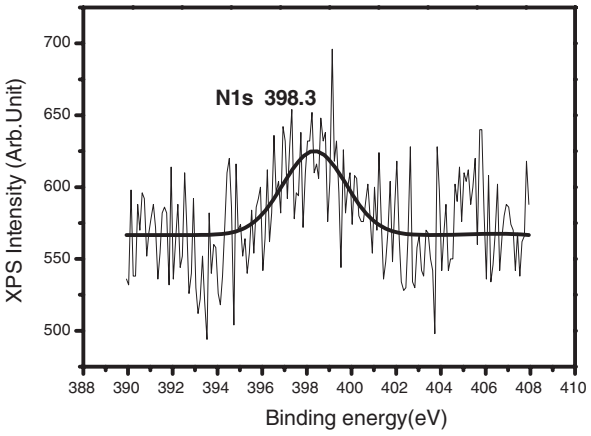

Fig. 5. The N1s XPS spectrum of catalyst Fe on Si wafer after pretreatment in NH_3.

of the nano-particles formed on the substrates (silicon). As the deposition angle decreased to 30°, the diameters of carbon nanotubes were more uniform with the increasing uniformity of catalyst particles.

On the other hand, there is a critical size of catalyst particles for the synthesis of carbon nanotubes [8]. When the particle size is larger than the critical size, they are not suitable for the growth of CNTs in the TCVD process. It is found that 90 nm of particle size is the critical size in our experiment. Therefore, according to the growth mechanism of CNT arrays [21], the presence of a large number of large particles more than 90 nm for 90° deposition angle inevitably decreased the density of carbon nanotubes resulting in worse alignment. With the deposition angle decreased, the large catalyst particles decreased and the small catalyst particles uniformly distributed on the substrates, resulting in an increase in the density of carbon nanotubes. Thus the carbon nanotube arrays showed better alignment.

The NH_3 pretreatment of catalyst films deposited for different deposition angles may affect their catalytic properties in the synthesis of carbon nanotubes. In order to clarify this effect, we examined the N1s XPS peak for Fe catalyst coated on silicon wafers after pretreatment (Fig. 5) in NH_3, which was fitted by a Gaussian line, with binding energy of 398.1 ± 0.2 eV. From Fig. 5, active N atoms or related radicals decomposed from NH_3 dissolved in catalyst particles after pretreatment. Further analysis showed that the N/Fe atom ratio increased from 0.12 to 0.17 (0.12 for 90° of deposition angle, 0.14 for 60° and 0.17 for 30°) with deposition angle decreased from 90° to 30°. This increase in N/Fe should be ascribed to the size distribution of the catalyst particles, since the pretreatment process in NH_3 proceeded using the same procedure. The presence of active nitrogen in the catalyst during CNT growth can increase the activation of catalyst and enhance carbon diffusion into the catalyst [22]. Jung et al. [23] also proposed that the role of nitrogen would be either to enhance the formation of graphite layer on the catalyst surface or to increase the separation of the graphitic layers from the catalyst. Therefore, the increasing content of N in the catalyst with a decrease in the deposition angle should be an important reason for the improvement of catalytic properties of the catalyst particles, resulting in a decrease of carbon particles in arrays. Pure carbon nanotube arrays were obtained for 30° of deposition angle.

4. Conclusions

The glancing deposition angle determined the morphologies of Fe films and hence the size distribution of Fe catalyst particles formed and the N/Fe atom ratio after thermal treatment in NH_3. More important, it affected the morphologies of carbon nanotube arrays synthesized. Therefore, the deposition angle of Fe films played a critical role in the synthesis of vertically aligned carbon nanotubes. When Fe catalyst produced at the deposition angle 30° was used to synthesize carbon nanotube arrays, pure carbon nanotube arrays with better alignment and uniform diameters were obtained.

Acknowledgments

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