Inventive design of Cu/SiO₂ substrate for chemical vapor deposition preparation of dense carbon nanofibers

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ABSTRACT

In this study, dense carbon nanofibers (CNFs) were prepared by CVD method on the surface of Cu/SiO₂ substrate. The Cu/SiO₂ substrate was fabricated by RF magnetron sputtering method. Firstly, the Cu atoms were sputtered to the surface of the SiO₂ substrate as the seed layer and the CNFs are planted on the seed layer by CVD technology. The CNFs with a diameter of 80 nm were prepared by this process. The CNFs prepared by this process get the advantages of small diameter, dense arrangement and high graphitization. These benefits are beneficial to the composite of multilayer materials. The preparation process remains steady, pollution-free and efficient, which breaks through the usual limitations of the preparation of CNFs. Direct preparation of CNFs on silica substrate is conducive to the application of integrated circuits and electronic devices.

1. Introduction

Carbon nanofibers (CNFs) are made of carbon atoms with a diameter of 10–500 nm and a length of 0.5–100 μm [1]. It is a one-dimensional carbon material, which has excellent physical, mechanical property and chemical stability, such as mechanism strength, electrical and thermal conductivity, etc. [2-4]. In recent year, many researchers have focused on the preparation of the CNFs, mainly including electrospinning method, chemical vapor deposition (CVD) method [5,6]. The electrospinning is an effective way to produce CNFs which has been widely used in electrochemical storage devices [7,8]. However, real mechanisms behind the electrospinning process are quite complex. In addition, using benzene and other toxic substances as carbon sources can cause pollution to the environment. Another approach to produce CNFs is CVD method. This method has been extensively used approach for industrial production of CNFs owing to its high controllability, high yield and ease of scale-up [9-11]. Different metal catalysts have been researched for preparation of CNFs, most of them being transition metal like nickel (Ni), titanium (Ti), iron (Fe), cobalt (Co) and so on [12-15]. Besides, numerous studies are further utilized alloys or organic materials as catalysts to prepare CNFs [16,17]. Mata et al. have used the Fast wet-chemical etching and hot filament chemical vapor deposition (HF/CVD) procedures to grow CNFs on copper (Cu) foils [18]. Md. Nasir Uddin et al. have used zeolite Y and methane (CH₄) as catalyst and carbon source to prepare CNFs on Ni substrate [19]. Amit Thakur have utilized the CVD method to prepare the coiled CNFs on stainless steel 304 (SS 304), stainless steel 316 (SS 316), Ni, and Inconel substrates [20]. In the meanwhile, carbon nanofibers prepared by CVD are widely used in microbial fuel cell [21], sterilization [22], adsorbent [23], power generation [24], electrode and other fields [25].

Based on the above references, the CVD process is one of the most effective methods for preparing CNFs and has been applied in many fields. In this study, we present a new way to prepare the dense CNFs on the surface of the SiO₂ substrate. We used the RF magnetron sputtering method to sputter the Cu atom on the surface of SiO₂ substrate as the seed layer and then use the CVD method to grow the dense CNFs on the surface of Cu/Si substrate. It can be concluded that the morphology of the seed layer of Cu atom plays an important role in the growth of CNFs. Compare to existing research, Muhammad Asif et al. reported synthesis of octopus-like carbon nanostructures (OCNS), which using a Cu catalyst via a conventional thermal CVD process, and this study also used the sputtering and CVD technology [26]. Through the system experiments, dense CNFs were achieved with a diameter of about 80 nm on the surface of SiO₂ substrate through the sputtering and CVD process. We analyzed the effect of cooling rate on the growth of CNFs and explained the growth mechanism. Morphology and quantification of Cu/SiO₂ substrate and CNFs were characterized by HRSEM and SEM + EDS. The CNFs have the advantages of small diameter and dense distribution without clotting by using this preparation method. This process was having the advantages of technology stability, high...
repeatability, non-pollution. The CNFs are prepared directly on isolated substrate, which can be utilized in the application of electronic devices.

2. Experimental

2.1. The preparation of Cu/Si substrate

The preparation process of CNFs consists of two parts. A layer of Cu atoms was sputtered on SiO\textsubscript{2} substrate by radio frequency (RF) magnetron sputtering system. During the sputtering process the RF power is set to 150 W and the sputtering time is 120 min. The substrate temperature of the sputtering process is 400 °C and the sputtering pressure is 1 Pa. Before the deposition process, the chamber was pumped by a mechanical pump and molecular pump vacuum system with the background pressure of about $10^{-6}$ Pa, the Cu (99.99%) target was cleaned for 30 min by sputtering in an argon atmosphere to obtain a steady vapor flow to the substrate. The seed layer of Cu atoms was sputtered on SiO\textsubscript{2} substrate by this process and we describe it as the Cu/SiO\textsubscript{2} substrate.

2.2. The fabrication of carbon nanofibers

The CNFs were planted on SiO\textsubscript{2} substrate by CVD method. The substrate temperature (T\textsubscript{s}) increased to 1000 °C in argon atmosphere. The heating rate was 8 °C/min during 0–800 °C and was set at 2 °C/min during 800–1000 °C. Argon (Ar) gas flow was 600 sccm in the heating stage. The Ar flow was adjusted to 1000 sccm when the T\textsubscript{s} is stable to 1000 °C, the flow rate of CH\textsubscript{4} and H\textsubscript{2} was 10 sccm and 100 sccm, respectively. Finally, the CNFs were obtained after rapid cooling process. In the cooling stage, we used a radiator fan to make the T\textsubscript{s} falling fast. As shown in Fig. 1, the T\textsubscript{s} is reduced for 42 °C/min during 1050 °C–600 °C, and then, the cooling rate is set at 25 °C/min during 600 °C–20 °C.

2.3. Characterization

Material phase analyses of Cu/SiO\textsubscript{2} substrate and CNFs were characterized by X-ray diffraction (XRD, Shimadzu 6100). The quality of CNFs was characterized by Raman spectroscopy (Renishaw inVia) with 514 nm laser excitation (∼2 µm spot size). The diameter of CNFs was characterized by high resolution scanning electron microscope (HRSEM, ZEISS SIGMA 300). The surface morphology and atomic percentage of Cu/SiO\textsubscript{2} substrate and the comparison of the growth of CNFs with rapid cooling were characterized by scanning electron microscope and energy disperse spectroscopy (SEM-EDS, Phenom ProX).

3. Results and discussion

Fig. 2a–c shows the SEM characterization of CNFs with different plotting scale. It can be observed in Fig. 2a, the growth of CNFs on the Cu/SiO\textsubscript{2} substrate is very dense, and the distribution density is relatively uniform without the phenomenon of clumping or tangling. Fig. 2b and c shows that the diameter of CNFs is about 70 to 80 nm. Through the analysis of the preparation technology can be found that the synthesis of CNFs requires two core elements. The first is the degree of dispersion of Cu atoms on the surface of SiO\textsubscript{2} substrate. The diameter of CNFs depends on the catalyst size and the catalytic activity of the catalyst to the carbon source. In order to ensure that the growth of the Cu seed layer more uniform, the SiO\textsubscript{2} substrate needs to maintain a rotation speed of one revolution per minute during the sputtering process. On the other hand, Cu is an active nonferrous metal that is easily oxidized in the air. Therefore, when the Cu/SiO\textsubscript{2} substrate is prepared, it should be put in the CVD system as soon as possible. Fig. 2d shows the Raman characterization of CNFs. Unlike traditional graphite materials, the Raman characteristic peak of CNFs has only two peaks at 1338 (D band) and 1591 (G band) cm$^{-1}$ [27], and the Cu signal makes the test curve produce a larger bulge. A low intensity ratio value of I\textsubscript{D}/I\textsubscript{G} value of the D and G band is used to evaluate the quality of CNFs [28]. The obtained I\textsubscript{D}/I\textsubscript{G} value here is 0.71, indicating the high gra-phitization of CNFs.

Fig. 3 shows the growth process of CNFs. Firstly, a layer of Cu atoms were prepared by RF magnetron sputtering method on SiO\textsubscript{2} substrate. The essence of sputtering technology is one way to provide vapor deposition. Magnetron sputtering technology is easy to control the film composition and thickness. The prepared film has good uniformity by using this technology [29]. These advantages are appropriate for large-area production of thin film. It is found that the surface state of Cu/SiO\textsubscript{2} substrate is a large-area island structure after sputtering process, where the activity of the top of the island is stronger than the bottom. Top of island is easier to absorb the carbon atoms in the deposition stage. Therefore, the deposition of carbon atoms becomes a kind of point deposition pattern rather than uniform deposition pattern in the CVD process and the CNFs continue to grow with the decomposition of the carbon source. The pyrolysis temperature of CH\textsubscript{4} is 700–1000 °C, and the melting point of copper metal is 1083.4 °C. The crystallization of carbon atoms deposited at low T\textsubscript{s} have a lot of defects in comparison to those deposited at higher T\textsubscript{s} [30]. Therefore, We set the T\textsubscript{s} to 1000 °C, which not only guarantees the cracking of the carbon source but also ensures that the Cu seed layer will not melt on the surface of SiO\textsubscript{2} substrate.

Based on the growth principle of thin film, we analyze the growth mechanism of CNFs. As shown in Fig. 4a, there are three growth modes of thin film, namely island growth model, layer growth model and mixed growth model. The growth mode of thin film is an island growth model in magnetron sputtering process. According to the above, the morphology of the CNFs was influenced by the morphology of the catalyst on the substrate. As shown in the Fig. 4b, the CNFs are grown on the substrate of Cu/SiO\textsubscript{2}, which has been sputtering 2 h, CNFs are uniform and dense. We increased the sputtering time to 6 h so that the Cu atoms covered the surface of the SiO\textsubscript{2} substrate as much as possible. After CVD process, the surface of the Cu/SiO\textsubscript{2} substrate does not grow out of CNFs, this is due to the sputtering time is too long, the morphology of Cu atoms on the surface of SiO\textsubscript{2} substrate is no longer a seed layer, it is a state of the film, as a result of the sputtering process was not in a high temperature environment, so the Cu film on the surface of SiO\textsubscript{2} substrate is not a stable crystalline state. As shown in Fig. 4c, the distribution of carbon atoms on the substrate surface is very chaotic. In the deposition stage of the carbon source, the Cu atoms on the surface of the substrate can still catalytically carbon source and makes the carbon deposition by means of atomic force adsorption to the surface, while the growth of carbon atoms is also a messy process. Therefore, we reduced the sputtering time to 4 h, and Fig. 4d shows the CNFs that were grown
on the surface of Cu/SiO₂ substrate, which was sputtered for 4 h. Compared with Fig. 4b, the growth morphology of growth result on the Cu/SiO₂ substrate is similar to a shape of the rod in Fig. 4d, and this result is also due to the excessive sputtering time. Through the system experiments and analysis, we can get the optimal CNFs growth consequence on the Cu/SiO₂ substrate, which was sputtered for 2 h.

At the end of the deposition stage, we use rapid cooling process to accelerate the crystallization of CNFs. As shown the photograph in Fig. 3, the heating unit is moved to the left until the bottom of the substrate is below the cooling fan when the deposition phase is over. The cooling fan can reduce the Tₜ rapidly and accelerate the crystallization of CNFs. Fig. 5 shows the effect of rapid cooling process for the growth of CNFs. Firstly, CNFs in Fig. 5a and b used the same experiment parameters during the deposition stage. Fig. 5a shows the CNFs without rapid cooling process (not moving the heating unit, not opening the cooling fan), it can be seen that the morphology of CNFs in Fig. 5b is different from the CNFs in Fig. 5a. Distribution of CNFs in Fig. 5a is messier. This is because the natural cooling slows down the crystallization rate of CNFs, which is a long annealing process that causes the crystallization of CNFs to become disordered. Therefore, the fast cooling stage in CVD process plays a key role in the crystallization of the CNFs. It also shows that the cooling rate has an influence on the crystallization of CNFs.

![Fig. 2. (a)–(c) The SEM characterization of CNFs with different plotting scale. (d) The Raman spectrum of CNFs.](image)

![Fig. 3. The growth process of carbon CNFs and the rapid cooling process of CVD system.](image)
morphology of CNFs.

Fig. 6a shows the XRD pattern and photo of Cu/SiO₂ substrate. The diffraction peaks of Cu atoms are at 43.3°, 50.43° and 74.13° respectively, the diffraction peak of Si located at 44.83° diffraction peak, this indicates the successful preparation of Cu/SiO₂ substrate. Fig. 6b shows the SEM characterization of the Cu/SiO₂ substrate surface. The surface state of the island structure composed of Cu atoms is clearly shown in this figure, and the Cu seed layer prepared by RF magnetron sputtering was relatively uniform. Fig. 7 shows the XRD pattern and photograph of CNFs. The color of CNFs on the Cu/Si substrate surface is close to off white. This is different from other carbon materials, such as transparent graphene film and diamond film, black graphite film and so on. By
comparing the XRD patterns in Figs. 6a and 7, it can be noted that the diffraction peaks of CNFs (002) are also found in the XRD curve of Fig. 7. To our surprise, no obvious diffraction peak of copper was discovered in the XRD curve in Fig. 7. Therefore, we characterized the atomic components of the substrate surface by EDS. Fig. 8a shows the EDS spectra and atomic percentage of CNFs sample. The results showed that the copper atomic percentage on the sample surface was only 0.2%, and the atomic percentage of carbon atoms and oxygen atoms was 30.6% and 65.7% respectively. The composition of oxygen on the substrate is more than twice that of Si. The ratio of composition of oxygen atoms to Si atoms in silica substrate is 2:1, which indicates that the extra oxygen atoms are adsorbed by CNFs. According to the mentioned above, the CNFs was widely applied in the field of adsorbent.

Fig. 7. The XRD pattern and photograph of CNFs on the Cu/SiO2 substrate.

Fig. 8. (a) The EDS spectra and atomic percentage of CNFs sample. (b) Map: silicon (resolution: 64 × 64 pixels). (c) Map: copper. (d) Map: carbon. (e) Map: oxygen.

4. Conclusion

In summary, the CNFs were prepared by two steps. Firstly, the Cu seed layer was prepared by using the physical vapor deposition process (RF magnetron sputtering) on SiO2 substrate, and then, the dense CNFs were prepared by CVD method on the surface of Cu/SiO2 substrate. A series of characterization and photographs can be proved that this process can be utilized to grow large-area CNFs directly on isolated substrate. The CNFs have the advantages of small diameter, dense growth and uniform distribution. These advantages are beneficial to the composite of multilayer materials and the application of multilayer devices. The preparation method is simple and suitable for the mass production. A new growth mechanism of CNFs was proposed by using this technique.
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