Optimized morphology properties of silver catalyst substrate for twisted carbon nanoribbon growth by PECVD method

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Abstract. A twisted carbon nanoribbon was deposited onto multicoated silver thin film using RF-PECVD method at relatively low radio frequency (rf) power, 8 watt. Plasma formation in the chamber is strongly influenced not only by rf power but also by methane flowrate hence in order to get optimum condition it need to be appropriated. At low rf power, deposited carbon atoms on catalyst substrate is obviously observed which is provides that even with a minimum power it still capable of resulted in carbon nanosheet but unable to enhance plasma formation therefore the properties of material absolutely need to be optimized. The fabrication process was carried out at 20 sccm of CH\textsubscript{4} for 20 minutes with 70 MHz/8 watt and 300 mTorr pressure. From SEM images it shows that the morphology of silver catalyst substrates determine carbon formation. Even-times coating of silver film able to reduced holes surface and more smoothing textures therefore suitable enough for carbon nanosheet medium.

1. Introduction

Synthesis of carbon nanomaterial via plasma enhanced chemical vapor deposition (PECVD) method still become attracting topic in thin film research and technology [1-6]. However it is not easy to control large area of carbon monolayer structure even unexpected either wrinkled or defect formation in material sheet is hard to be prevented [4-5]. Several parameter are strongly responsible on interatomic bonding when chemical reaction has been happen. For instance, the overdose thermal treatment is going to degradate the structure both in atomic position and vacancies which is would lead to decrease the electronic properties of material. Whereas appropriate thermal energy is required to repair structure [6]. In addition enhanced plasma in the chamber is needed to get better structure meanwhile only less deposited carbon atoms can be produced, so there are some problems that need to be overcome. Furthermore the quality of thin film nanomaterial fabricated on catalyst substrate is also depend on morphology properties. Carbon nanosheet (CNS) on single crystal substrate was resulted in better structure compared with polycrystal [7]. Therefore it is necessary to fabricate a suitable catalyst as a first step before the growth of nanomaterial sheet such as nanoribbon, this material can be developed into CNT that can be applied in any electronic device.

In this study, the morphology properties of silver thin film for carbon nanoribbon fabrication has been discussed. The RF-PECVD hot wire cell assisted with very high frequency was performed to...
fabricate carbon nanomaterial at relatively low temperature system, it is works only at lower than 300 °C where from previous reports several researchers used higher [8-9]. In order to compensate this low thermal operating system it can be used low pressure condition under millitorr scale. High vacuum condition not only enable to result in different surface potential of carbon sheet but also the number of graphene layer [10], on the other hand the number of metal thin film coating for substrate catalyst [11] also need to be considered because of stability formation of carbon influenced by the substrate quality. When the number of stuck layer increases more than tens hence it can not defined as graphene anymore consequently all electronic properties are far enough from carbon nanomaterial. Besides, each of operating system parameter is almost useless if the medium for carbon growth has not proper characteristic hence one of the most important thing is optimizing the morphology of the medium in order to acquire an expected result.

2. Experimental Method
Few parts (0.0342, 0.018, 0.015 and 0.014 gram) high purity silver pellets (99.99%) with 0.1 mm thickness and 0.7 cm diameter wide were evaporated on glass substrate forming metal thin film prepared by physical vapor deposition method then repeated until four times to get multilayer silver film. Each of them was evaporated piece by piece under vacuum condition resulted in four types of silver films (single, double, triple and quardple coating). This metal substrates is called as catalyst for carbon growth medium.

The SEM measurement was performed to observe surface, morphology and also grain boundary properties of the sample then it put into PECVD chamber at the same time. The growth parameters were set up at 70 MHz/8 watt under 300 mTorr pressure with 250 °C substrate temperature. Methane flux introduced at 20 sccm for 20 minutes (taken into account after orange color of plasma turned up and clearly observed from window port of the chamber. Deposited carbon nanosheet on the catalyst silver films was investigated by Raman spectroscopy (Bruker, Inc. at λ = 523 nm laser source) to analyzed the quality of material at obvious looked sample.

3. Result and Discussion
In general, someone can uses high quality single crystal structure of transition metal foil as substrate that can easily to be found in several companies, it can be ordered then purchased via online but certainly it more expensive compared with self-production. In this study, it was used silver film as catalyst substrate which was fabricated via simple physical vapor deposition then annealed to fine its structure forming single crystal like structure. It only need several miligram of metal precursor to make teen substrate samples so this method is claimed more effective and proper to be developed. Based on XRD characterization the 600°C thermal treatment for 30 and 60 minutes samples have polycrystal structure with the (111) crystal direction at 2θ = 38° which is more dominant compared with others while the (200) at 2θ = 44.26° and (222) at 2θ = 81.85° hence it has only one particular direction. The (111) direction is profitable for CNS growth owing to the interatomic bonding of carbon will follow this path. The intersection of crystal direction create a grain boundary on the surface that may disturb CNS formation mechanism. Typical SEM images of silver catalyst on the substrate fabricated via PVD are given in Figure 1. The evaporated precursor in gases phase is spreading out onto the glasses which is positioned on the top of metal boat. The glasses would completely coated by this metal in order to create substrate catalyst. Morphology of glass is strongly influences the quality of the catalyst in addition the coating process will follow as rough as the contour of the surface. Commonly, a conventional glass has high roughness properties consequently it need to be set up to result in smoothest profile. The most-simple step is by thermal treatment but due to the weak of atomic bonding of the metal at outer surface so a lot of deposited metal back to realeased from the glass. Figure 1a. Shows the presence of vicinal porous caused by re-evaporation. Another step is multicasting treatment by repeating deposition process to get thick catalyst metal in order to repairing this surface. Second coating treatment resulted in better surface (Figure 1b) while for fourth treatment the surface become back to initial condition.
Figure 1. Vicinal porous of one to four multicoated silver thin films on glass substrate. (a) one, (b) twice, three times and (d) four times coating. Even coating treatment is more smoother than the odd one.

Figure 2. Raman image (left) and its spectra (right) of carbon ribbon deposited on annealed silver films.

Actually graphene layers on metal surfaces can be prepared by two methods, that are by the segregation of bulk dissolved carbon and by the decomposition of carbon containing molecules, but the most popular method is the second one (e.g. CVD). However the CVD method is more powerful to produces high quality thin film, provided with two dimensional materials in application for electronic device prefer to use this method. In fact, graphene is a multifunctional material which has been developed from time to time. In term of fabrication process via CVD method it need a catalyst substrate as guidance growth. There are several metals transition can be performed, whatever the metal is, the carbon solubility in surface metal need to be considered due to it going to restrict monolayer sheet of carbon formation. Since high solubility of metal, the surface carbon gradually going to dissolves into the catalyst when the surface completely covered so the growth is terminated. On the other hand, it need single crystal catalyst substrate with no grain boundary on the surface therefore the
inter-bonds of carbon able to arrange perfectly to get graphene large area. The deposited carbon onto substrate going to insert inside then moving up to the surface to form inter-atomic bonding but this valid only for carbon atoms that have quite energy and not for all of the diffused carbon atoms. For atoms with less energy, it will stay inside to fill an empty space to make a mixture. In addition the growth of both monolayers and multilayers can be controlled by the temperature, when high energy from thermal treatment is more absorbed, the carbon in the empty space may dopes the substrate hence it can not be called has similar structure with standard catalyst substrate anymore. The structure is absolutely changes due to the present of other atoms therefore the re-usage of substrate is not recommended for functional nanomaterials growth.

Raman image includes its spectra characterization presented in Figure 2 show two peaks centered at 1329 and 1592 nm which are assigned to the D and G modes of CNS respectively. The appearance of the D peak is attributed to the defects or structural disorder which is not observed for a perfect graphene sheet [12]. The intensity ratio of the D to G peaks in the Raman spectrum of graphene has been shown the degree of disorder in the sheets [13]. The defects including vacancies and distortions may be attributed to non-uniformity, corrugation and twisting in CNS [14]. There are three types of CNS, graphene as large area carbon nanosheet, carbon nanoribbon and twisted carbon nanosheet or nanoribbon. Twisted sheet of carbon nanomaterial is contributed by external energy such as thermal or mechanics. In CVD chamber, the substrate port has quite thermal energy to fine thin film structure but inappropriate energy that given to material will disturb the structure itself. In addition, the source of methane flow valve position is strongly influences the type of CNS. Horizontal direction will resulted in ribbon sheet while the vertical one will resulted in large area sheet. Nevertheless this direction is also strongly influenced by outlet valve position so there are many parameter need to be considered in order to generate expected material. The CNS can be growth on minimum porous of catalyst substrate, twice coating treatment is recommended enough in order to fabricate of CNS as shown in Figure 2.

4. Conclusion
Twisted carbon nanoribbon has growth via PECVD at relatively low temperature using multicoated silver thin film. Even coating treatment is recommended for catalyst substrate fabrication due to the morphology properties of the surface more smooth compared with the odd one. In addition, repairing structure of metal thin film by applying appropriate thermal has done to get dominant crystal direction particularly in (111). This thermal energy has contributed on twisting phenomena

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