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Graphene film synthesized by electron beam irradiation on PVDC

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1. Introduction

Graphene is an ideal two-dimensional material backboned with sp2-hybridized carbon atoms and draws significant interest due to its superior electrical properties represented by its high carrier mobility and its remarkable structure stability [1,2]. Based on these excellent characteristics, graphene is assessed as a material with unlimited potential for practical uses [2]. Since its first isolation by mechanical exfoliation [3], various techniques have been developed for the synthesis of graphene, such as epitaxial growth from silicon carbide, chemical reduction of graphene oxide, and chemical vapor deposition(CVD) on transition metal substrates [1].

However, mechanical exfoliation and epitaxial growth on silicon carbide have limitation for synthesis the large area graphene due to its quality, shape and size. While large scale and high quality graphene can be synthesized by CVD process [4], thus the CVD process has become a dominant method in graphene production. Nevertheless, in the case of CVD, there is also disadvantages that there are a risk of explosion by using a combustible gas at a high temperature around 1000℃ and it needs complicated process such as preparation, growth, cooling, and transference [1]. Therefore, a relatively safe synthesis method is required rather than the existing production process.

Miller, A.A. reported that the structure of PVC (Polyvinyl chloride) film was changed when irradiated at high energy electron beam [5]. During irradiation process, C-Cl bond in PVC was broken and carbon radical was produced due to high energy beam. Then, long chain of hydrocarbon was created by bonding the carbon radicals together.

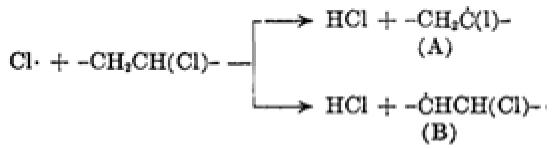

Fig. 1. Structural change of PVC during electron beam irradiation

In radiation process, break and creation of chain are called scission and crosslinking. After irradiation, polyene and aromatic ring, which are the foundation of graphene, could be created through scission and crosslinking of polymer by radiation. Thus, graphene can be made by controlling the degree of polyenes and aromatic rings with controlling the amount of electron beam. However, this process is hard to use at industries because of its high energy. Herein we report that graphene like-carbon is created in PVDC (Polyvinylidene chloride) through low energy electron beam irradiation. Since PVDC has 2 C-Cl in skeletal formula, thus more aliphatic carbon and aromatic rings could be formed after irradiation. Moreover, irradiation process doesn't require many process & chemicals in synthesis of graphene, but it is more safety than other synthesis method because it is performed at room temperature. The 50keV electron beam device manufactured by our laboratory is used and the generation of graphene like-carbon is confirmed through the Raman spectrum.

2. Methods

2.1. Sample preparation

In the considered experiments, 15 μm and 33 μm PVDC film (Goodfellow) were prepared. Titanium (Ti) substrate was cut by 2×2 cm^2, then it was sonicated in an acetone and ethanol solution (99%, Sigma Aldrich) for 10 minutes to remove impurities. Even after, impurities and dust in substrate were removed using N2 gas air gun. After that, the ethyl alcohol solution was dropped about 2-3 drops to serve as an adhesive between the Ti substrate and PVDC film, then PVDC film was completely adhered to the titanium substrate so as not to bubble. After that, remained ethyl alcohol was vaporized by using dryer, finally, nitrogen gas was blown out by air gun to remove impurities.

2.2. Electron beam irradiation on polymer & Raman

In this paper, 50keV electron beam device produced in our lab was used. Each experimental condition is shown in the table 1. The PVDC sample was fixedly placed in the electron beam irradiator, and then the inside of the irradiator was evacuated. At this time, the degree of vacuum was maintained at 10^{-6} Torr by using a rotary pump and a turbo pump. Then, electron beam was irradiated to the PVDC sample by controlling the current and the electron beam irradiation time in each experimental condition. After irradiation, synthesized graphene film was characterized by a Raman spectrometer (514.5nm laser, ARAMIS, Horiba Jobin Yvon).

Fig. 2. 50 keV electron beam device

	1	2
Fluence(x10^{16}#/cm^2)	1.788	10.7
Absorbed Dose (MGy)	5.791	34.748

Table 1. Experimental condition of each sample

3. Results and discussion

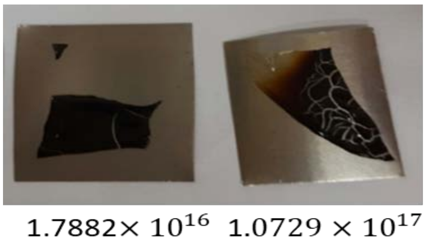

Fig. 3. Optical image of PVDC film of 15 μm irradiated on a) first condition & b) second condition.

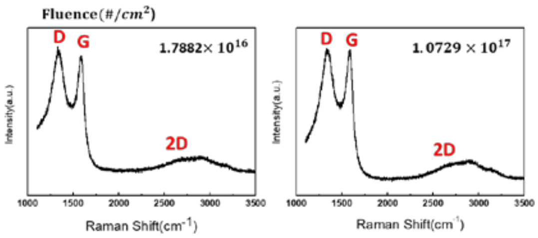

Fig. 4. Raman spectra of PVDC film of 15 μm irradiated on a) first condition & b) second condition.

The optical image of PVDC film of 15 μm after irradiation were shown in fig. 3. After irradiation, the transparent PVDC film was changed into opaquely and turned black. Especially, PVDC film irradiated on second condition was split, which appears to result from the film being shrunk and cured by the electron beam. The Raman spectra of PVDC after electron beam irradiation at each condition was shown in Fig. 4. These spectrums show the sharp D band at 1350 cm^{-1}, G band at 1600 cm^{-1} and broad 2D spectrum between 2600 and 2900 cm^{-1}. It means the graphene-like carbons were synthesized in irradiated PVDC. Also, the intensity ratio of D to G peak decreased as the absorbed dose increased and it indicated that the crystallinity of irradiated PVDC increased.

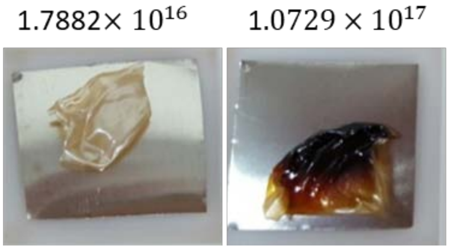

Fig. 5. Optical image of PVDC film of 33 μm irradiated on a) first condition & b) second condition.

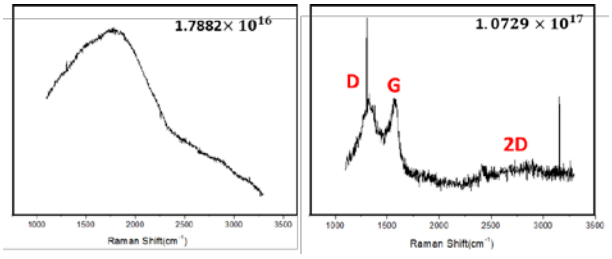

Fig. 6. Raman spectra of PVDC film of 33 μm irradiated on a) first condition & b) second condition.

The optical image of PVDC film of 33 μm after irradiation were shown in fig. 5. After irradiation, irradiated samples were bent. Furthermore, D, G and 2D peak weren't appeared in the Raman spectra of PVDC irradiation on first condition (Fig. 6a). Although the D and G peak were shown in Fig 6b, but 2D peak were not appeared. Electron beam irradiation changes the surface structure of the film. When an electron beam was irradiated on a thick PVDC film, only the very thin surface of the film would be changed. However, the degree of shrinkage of the changed surface and the existing PVDC film are different, thus the thick PVDC film was bent during irradiation process. In the case of thin PVDC film, structure of almost films were changed then the PVDC film after irradiation were not bent.

In conclusion, PVDC film of 15 μm irradiated on first condition is the best solution to optimize fabrication of uniform graphene film.

4. Conclusions

Graphene has been evaluated as a next generation material due to its superior electrical properties compared to conventional materials. However, conventional methods to synthesize graphene have many disadvantages in commercialization so a new method is required. We have presented a facile route to graphene film by irradiation on PVDC film.

Raman spectra of PVDC film irradiated with electron beam shows that generated material in PVDC film by electron beam has the characteristics of graphitic material having defects. Besides, the degree of graphite increases more as the electron beam dose increases. However, much data is required to optimize the experimental condition. To summarize, PVDC film of 15 μm irradiated on first condition is the best solution to fabricate the uniform graphene film in this paper and more data should be required to optimize the condition of electron beam.

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