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Synthesis of graphene nanosheets from indium-catlyzed graphite using electron beam irraditaion

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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]. Especially, grapehen nanosheets, two-dimensional (2D) carbon nanostructures consisting of few graphene layers and open surfaces and edges, have attracted the attention of researchers. The graphene nanosheets have the high surface volume ratio due to its sharp edges and open structures, and it can be advantage for electrical applications such as gas detection, gas storage and batteries that are required high electrical mobilities [3]. The conventional methods to synthesize graphene nanosheets are chemical vapor deposition (CVD), electrophoretic deposition, salt-tmeplating methods [3]. However, these methods have still limitation because of difficulties in the preparation of large scale, dense graphene nanosheets.

Here, we present a simple and convenient route to synthesize the graphene nanosheets by electron beam irradiation to indium (In) and graphite mixture. In previous research, we provided that indium is a catalyst for degradation and combination of graphite. In vacuum furnace, graphite was degraded by the indium catalyst at high temperature. Furthermore, carbon atoms from degraded graphite are rearranged to graphene nanosheets by indium catalyst [3]. In spired by these, we tried to fabricate graphene nanosheets from indium-catalyzed graphite using electron beam irradiation. When an electron beam is irradiated, the electron beam gives heat and a large amount of energy to mixed graphite and indium, thus indium is easily activated to degrade the graphite and combine the carbon atoms into graphene. This process doesn't need high pressure gas and temperature, so it is more safety than other synthesis methods. In this study, 2 types of indium, sputtered In and In particles, was used to fabricate the graphene nanosheets to determine the appropriate In catalyst type. The 50keV electron beam device manufactured by our laboratory is used and the morphology of graphene nanosheets are confirmed through the scanning electron microscopy (SEM).

2. Methods

2.1. Sample preparation

Before the irradiation process, to fix the graphite to the substrate, graphite-1, 2-dichlorobenzene solution (0.3 wt% graphite) was prepared. Graphite solution of 5μl was dropped on the silicon (Si) substrate then the substrate with graphite solution was dried for 30 minutes to vaporize the 1,2-dichlorobenzene. After that, two types of In catalysts, sputtered In and In particles, were stacked on the graphite particles. In the case of graphite with sputtered indium, indium-sputtering process (currents: 40μA) was performed during 30minutes after drying graphite solution. In the case of graphite with indium particles, indium particles of 0.025g were dropped on the substrate, then 1, 2-dichlorobenzene of 5μl was dropped to substrate to fix the indium particles.

2.2. Electron beam irradiation & SEM observation

In this paper, 50keV electron beam device produced in our lab was used. Each experimental condition is shown in the table 1. The Si substrate 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 mixture of graphite and indium by controlling the current and the electron beam irradiation time in each experimental condition. After irradiation, morphology of synthesized graphene nanosheets was observed by a scanning electron microscopy (S-4800, HITACHI, Japan).

	1	2
Beam currents (μA)	80	200
Irradiation Time (min)	30	30
Fluence($x10^{16}$#/cm^2)	3.06	7.63
Absorbed Dose (MGy)	9.91	24.71

Table 1. Experimental condition of each condition.

3. Results and Discussion

The morphologies of indium catalysts before irradiation process are shown at Fig. 1. The size of indium particles were measured through SEM image, the size range of indium particles are revealed to 10-100nm.

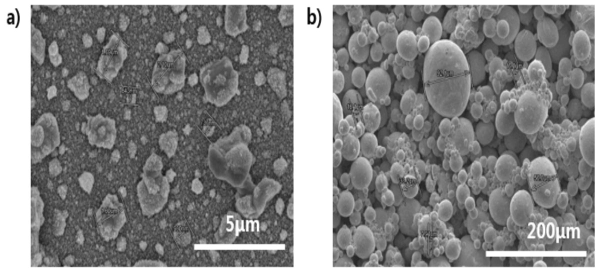

Figure. 1. a) Spputered indium on Si substrate and b) indium particles on Si substrate before electron beam irradiation

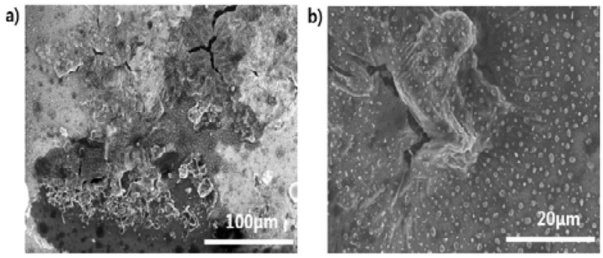

Figure. 2. The SEM image of sputtered In on Si substrate after electron beam irradiation at condition 1. the scale bar size of a) is 100um and b) is 20um

Fig. 2. is a SEM image of sputtered In on Si substrate after electron beam irradiation at condition 1. As shown in Fig. 2, the indium particles still cover the graphite, and indium migrated compared with fig. 1. a), but no graphene nanosheet was observed in these images.

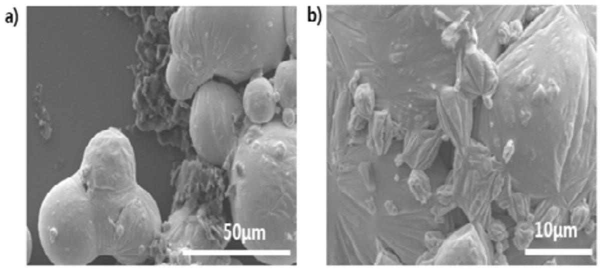

Figure. 3. The SEM image of In particles on Si substrate after electron beam irradiation at condition 1. the scale bar size of a) is 50um and b) is 10um

Fig. 3. is SEM image of In particles on Si substrate after electron beam irradiation at condition 1. As shown in Fig. 3., the traces of melting of the indium particles were observed but there are no any morphology of graphene nanosheet in figure. It is assumed that the electron beam energy was too low to active the indium catalysts. Thus, the beam currents increased into 200μm (condition 2) synthesis was performed by this condition.

Fig. 4. is the SEM image of sputtered In and fabricated graphene nanosheets on Si substrate after electron beam irradiation at condition 2. The corrugated film structure is estimated to be a graphene nanosheets (fig 3. a)). The thickness of this film as shown in fig. 3. is assumed that less 100nm. Also,

After the electron beam irradiation, the sputtered In almost disappeared on the substrate.

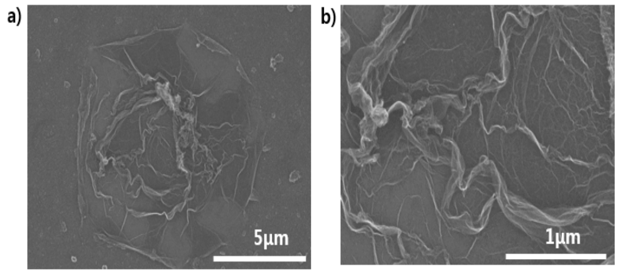

Figure. 4 The SEM image of sputtered In on Si substrate after electron beam irradiation at condition 2. the scale bar size of a) is 5um and b) is 1um

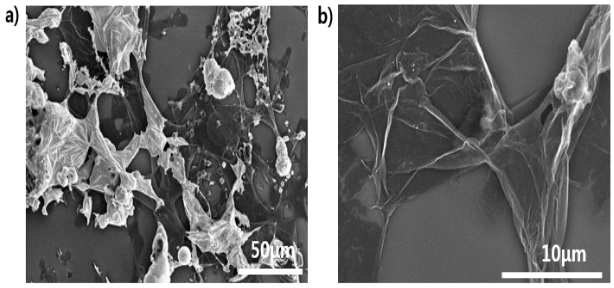

Figure. 5. The SEM image of In particles and graphene nanosheets on Si substrate after electron beam irradiation at condition 2. the scale bar size of a) is 50um and b) is 10um

Fig. 4 is the SEM image of In particles and graphene nanosheets on Si substrate after electron beam irradiation at condition 2. As shown in Fig. 5. a), still indium particles remained after the electron beam irradiation, but particle sized decreased and graphene nanosheets are formed around the remained indium particles. Furthermore, the thickness of fabricated graphene nanosheets were assumed that few micrometers. However, the thick graphene nanosheets is a disadvantage to adapt at industrial field, because too much thick graphene nanosheets hinder the carrier mobilities. Besides, remained In particles can be the impurities of graphene nanosheets.

To summarize, when tested under the same conditions, using sputtered In rather than using In particles can produce higher quality graphene nanosheets. However, a few experiments at each condition were conducted in this paper. Thus, more data of graphene nanosheets synthesis with electron beam irradiation at various condition is required to synthesize the high quality graphene nanosheets.

4. Conclusion

Graphene nanosheets has been attracted to researchers 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 new method to synthesize the graphene nanosheets from indium-catlyzed graphite using electron beam irradiation . SEM image of each In catalysts after electron beam shows that In order to synthesize a graphene nanosheet, a beam current higher than a certain level is required. Moreover, it is revealed that sputtered In is better than In particles to fabricate the high quality graphene nanosheets. In the case of In particles, In particles still remained after synthesis process, and fabricated graphene nanosheets were too thick. However, much data is required to optimize the experimental condition. To summarize, graphene nanosheets would be synthesized with electron beam as controlling the absorbed dose and more data should be required to optimize the condition of electron beam.

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