# A Study on Synthesis Mechanism of Graphene Quantum Dots by Ion-beam assisted Chemical Vapor Deposition

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## 1. Introduction

A fantastic two-dimensional (2D) carbon material, graphene, has recently attracted remarkable attention due to its wide range of possible applications in transistors, supercapacitors, gas sensors, solar cells, and flexible displays [1-5]. Because of its promising potential applications, not only graphene but also graphene based nanostructures such as graphene nanoribbons and epitaxial graphene have been also widely studied. Graphene quantum dots (GQDs) which indicate graphene sheets less than tens of nanometer attracted researchers because they exhibit unique optical and electronical properties due to quantum confinement and edge effects. GQDs have many advantages compared with other carbon nanomaterials because they have outstanding biocompatibility, low toxicity, good solubility, and high surface area which lead them to have versatile applications: sensors, bio-imaging, drug delivery, and photo-catalysts [6-14].

Generally, GQDs are formed through top-down approaches by cutting, exfoliation, and cage-opening carbonic precursors such as graphite, graphene, graphene oxide, fullerenes, and carbon fiber, into smaller pieces using chemical methods. The methods have their unique advantages, but they typically require the use of strong oxidants (such as KMnO4 and KClO3) and acids (such as H2SO4, HNO3, and HCl) which limited GQDs (synthesized by conventional chemical methods) to apply to utilization in bio-fields. Furthermore, currently, there is still no universal approach for the preparation of GQDs without byproduct and well-size and property controlled GQDs. [15-19]

Here, we present a study on synthesis mechanism of GQDs by ion-beam assisted chemical vapor deposition (CVD) at Korea Multi-purpose Accelerator Complex (KOMAC). Ion-beam assisted CVD is a simple and convenient route to highly pure GQDs. After fabrication of GQDs, only GQDs remained without any impurities and byproducts. Additionally, the size and properties of GQDs are easily controlled by changing the conditions of ion-beam irradiation and thermal annealing.

## 2. Methods and Results

In this section, the detailed procedures of the study on synthesis mechanism of GQDs by ion-beam assisted CVD are described.

### *2.1 Fabrication procedures of GQDs by ion-beam assisted CVD*

The overall synthesis approach is illustrated in Figure 1. Catalysts for the GQD fabrication are provided on polished Si substrates by ion-beam irradiation. Ion-beam irradiated Si substrates were annealed at higher than 700℃ for 20 min under Ar atmosphere, and then nano-sized catalysts were produced on the Si substrate. GQDs were synthesized at the nano-sized catalysts using methane gases (carbon source). After GQD fabrication, the nano-sized catalysts were totally removed due to a high temperature, and only pure GQDs remained on the Si substrate.

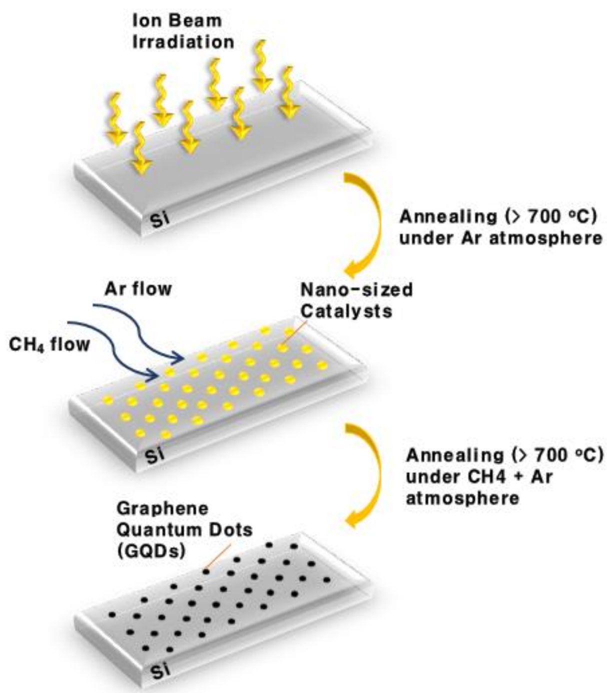


Fig. 1. A schematic of fabrication procedures of GQDs by ion-beam assisted CVD method.

### *2.2 Synthesis mechanism of nano-sized catalysts and GQDs*

Catalyst ions were implanted into the specific depth of Si substrate by ion-beam irradiation. Then, during an annealing process, the inserted ions are diffused to the surface of Si substrate, and simultaneously the ions are aggregated each other, then nano-sized catalysts are formed on the Si surface (Figure 2). Under prolonged annealing process, additional ions are combined with aggregated catalysts on the Si surface and larger-sized catalysts are fabricated.

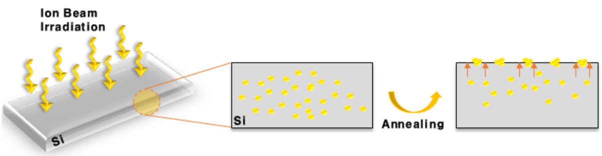


Fig. 2. A schematic of synthesis mechanism of nano-sized catalysts.

Figure 3 shows cross-sectional and magnified high-resolution transmission electron microscope (HRTEM) images of ion-beam irradiated Si (Fig. 3a) and annealed Si (Fig. 3b) substrates, respectively. After Fe ion beam irradiation, very small sized (~ less than 1 nm) Fe ions or particles were uniformly dispersed near the Si substrate. But after annealing process with Ar gases, Fe ions were aggregated each other and most Fe aggregates were placed on the surface of Si substrate or very near the Si surface.

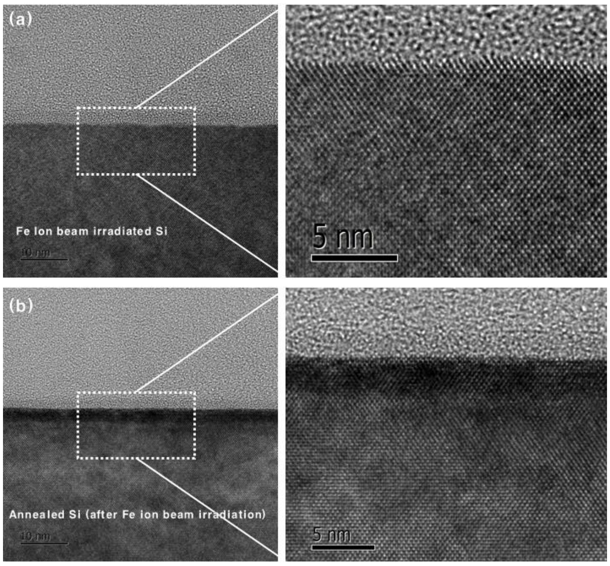


Fig. 3. Cross-sectional and magnified HRTEM images. (a) the Si substrate irradiated by Fe ion beam, (b) the Si substrate annealed after Fe ion beam irradiation.

Figure 4 shows atomic force microscope (AFM) images of the nano-sized catalysts fabricated by ion-beam irradiation at different fluences. After annealing process with Ar gases, smaller sized and amounts of catalysts were fabricated at low fluence (5 x $10^{14}$ ion/cm$^2$) of ion beam irradiation condition. On the other hand, larger sized and amounts of catalysts were formed at high fluence condition (5 x $10^{16}$ ion/cm$^2$). It means that the size and amount of catalyst could be easily controlled by changing the condition of ion beam irradiation.

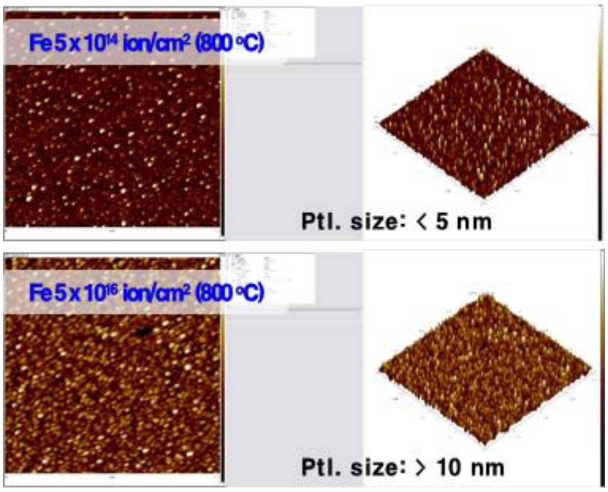


Fig. 4. AFM images of catalyst fabricated at different fluence of ion beam irradiation.

Using nano-sized catalysts, GQDs are synthesized by an annealing process under CH4 and Ar atmospheres. The size of GQDs could be controlled by changing flow rates of CH4 and Ar gases. Figure 5 exhibits the GQDs synthesized by ion-beam assisted CVD method.

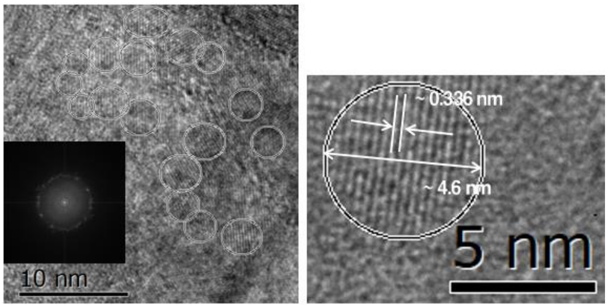


Fig. 5. HRTEM images of GQDs synthesized by ion-beam assisted CVD method.

## 3. Conclusions

The synthesis mechanism of GQDs by ion-beam assisted CVD was studied using various analyzing devices such as HRTEM, FESEM, EDX, AFM, Raman, XPS and so on. Formation and size of catalysts could be controlled by changing the condition of ion beam irradiation and annealing process. This catalyst control has also a decisive effect on the GQD synthesis.

## 4. Acknowledgement

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