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STUDY OF GRAPHITIZATION BEHAVIOR OF METAL-ION IMPLANTED PRECURSOR POLYMER

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Introduction

It is well known that the catalytic graphitization by metal-nanoparticles of Fe, Co, Ni, and so on, enables formation of graphitic structure from precursor polymers at relatively low temperature range of 800-1000ºC. It has been reported that the graphitization behavior depends on the size of metal-nanoparticles; a turbostratic graphite structure is formed in the case of that the particle size is below 20 nm [1]. It is said that the turbostratic graphite structure is necessary to fabricate carbon materials with catalytic performance, for example, nitrogen (N)-doped carbon catalysts [2]. In many cases, the N-doped carbon catalysts have been fabricated by pyrolysis of the blends of precursor polymers and/or metal-compounds, however, there are few reports on fabrication of the N-doped carbon catalysts with controlling the size of metal-particles. If the size of metal-particles is controlled below 20 nm, it is expected that the N-doped carbon catalysts with higher activity can be fabricated. On the other hand, ion implantation technique possesses selectivity of various ion species, controllability of ion energy and fluence (number of ions). The size of metal-particles can be potentially controlled in the range of below 20 nm by utilizing the ion implantation technique because this technique is based on a "bottom-up" process. Thus, the ion implantation technique would be useful to fabricate the turbostratic graphite structure in high efficiency. In this work, a phenolic resin was implanted by 100 keV Fe^+ ions and subsequently carbonized in order to investigate the formation of Fe particles and the performance of formed Fe particles as the catalyst for the graphitization of the phenolic resin.

Materials and Methods

A phenolic resin which is coated on a Si wafer with thickness of about 5 μm was subjected to the implantation of 100 keV Fe^+ ions with fluence of 1×10^{16} ions/cm^2 as the maximum under vacuum at ambient temperature. After the implantation, the non-implanted part of the phenolic resin was dissolved by immersing into methanol. The exfoliated sample with thickness of about 200 nm was heat-treated at 800ºC in a nitrogen gas atmosphere (Figure 1). The obtained carbon materials were investigated by transmission electron microscope (TEM).

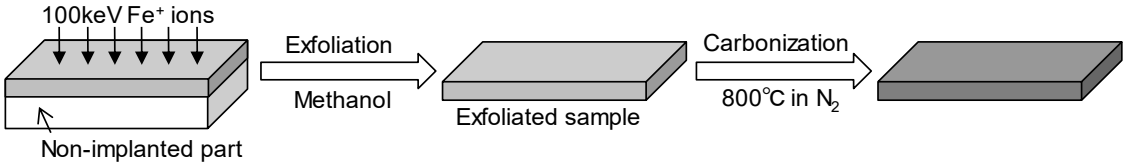

Figure 1. Procedure of sample-preparation in this work.

Results and Discussion

The implanted Fe^+ ions are reduced to Fe atoms through the reaction with secondary electrons generated in the phenolic resin: $Fe^+ + e^- \rightarrow Fe$. The Fe nanoparticles were not formed just after the implantation in the TEM observation. The Fe nanoparticles were found in the carbon material after the heat treatment at 800 ºC. Figure 2 shows relationship between mean size of Fe nanoparticle in the obtained carbon material and fluence of 100 keV Fe^+ ions. The mean size of Fe nanoparticle was 7.6±2.4, 12.8±3.7, 19.6±5.7, 26.4±8.5 nm for the fluence of 1×10^{14}, 5×10^{14}, 1×10^{15}, 1×10^{16} ions/cm^2, respectively. Any particles with the size of more than 50 nm were not observed. This result suggests that the size of Fe nanoparticle can be controlled by the fluence of Fe^+ ions in the range of 5-30 nm.

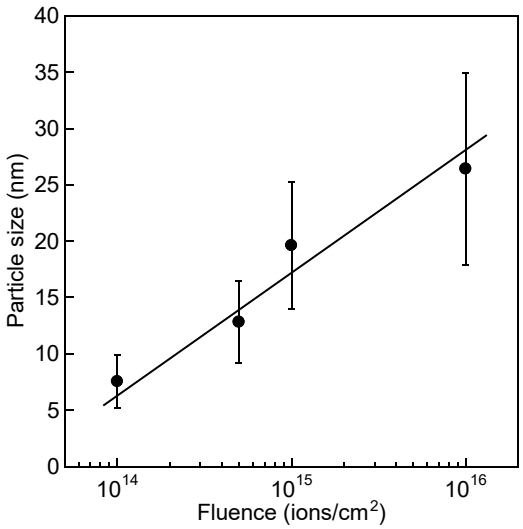

Figure 2. Relationship between mean size of Fe nanoparticle in the obtained carbon material and fluence of 100 keV Fe^+.

While featureless amorphous texture was observed in the case of the carbon material without Fe^+ ion implantation, the turbostratic graphite structure was observed around the Fe nanoparticles in the obtained carbon materials with the fluence above 5×10^{14} ions/cm^2 in the TEM observation. This indicates that the implanted Fe^+ ions are effective for the catalytic graphitization of the phenolic resin to form the turbostratic graphite structure.

Conclusions

In this work, a phenolic resin was implanted by 100 keV Fe^+ ions under vacuum at ambient temperature and carbonized at 800ºC under the nitrogen atmosphere in order to investigate the formation of Fe particles and the performance of formed Fe particles as the catalyst for the graphitization of the phenolic resin. And the following concluding remarks were obtained.

(1) The Fe nanoparticles were formed in the fabricated carbon material utilizing the Fe^+ ion implantation into the phenolic resin and subsequent carbonization.
(2) The size of Fe nanoparticle can be controlled by the fluence of Fe^+ ions in the range of 5-30 nm.
(3) The implanted Fe^+ ions are effective for the catalytic graphitization of the phenolic resin during the carbonization process to form the turbostratic graphite structure.

Acknowledgment

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