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学位論文題目	Low Temperature Growth of Graphene Using Low Melting Point Metals （低融点金属を用いたグラフェンの低温合成）

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論文内容の要旨

Graphene, a two dimensional allotrope of carbon in a honeycomb lattice, has gathered wide attention due to its excellent electrical, thermal, optical and mechanical properties. Conventional synthesis methods, such as chemical vapor deposition (CVD) method, require a high temperature for its growth. Thus the development of the low-temperature growth is still challenging.

In this thesis, it is successfully demonstrated that the melting point of the catalyst metal plays an important role to achieve the low temperature growth of graphene, based on the high-resolution transmission electron microscopy (TEM) observation of the graphitization process. In order to achieve the low temperature graphene growth, two strategies were attempted for the selection of the catalyst; one is using the low melting point metal as the catalyst and another is using the nano-sized particles to lower the melting point of the metal.

Encouraged by the previous success in the graphene growth at 250°C using novel catalyst, Sn, in our group, indium (In) whose melting point is much lower than Sn was attempted as the catalyst here. In order to observe the local graphitization by TEM, In- included

carbon nanofibers (In-CNFs) were fabricated on an edge of a carbon foil by Ar^+ ion sputtering of both the carbon foil and an In plate. Depending on the ion energy, graphitization catalyzed by In was observed even for the as-sputtered sample without post annealing, suggesting that In is promising as the catalyst for the low temperature graphene growth. Based on this fact, a stacked film of In and amorphous C was deposited onto a SiO_2 covered Si substrate, and this thin film sample was then annealed in vacuum at 150 and 200°C. In both cases, clear 2D peak in Raman spectra, which is the evidence of the graphene formation, was observed.

In order to check the temperature dependence of catalytic activity in local graphitization for nano-sized catalyst, CNFs including Sn nanopartilces (Sn-CNFs) prepared by the ion sputtering method were annealed in vacuum at 180 and 250°C. The Sn-CNFs was characterized by the dispersion of Sn nanoparticles 2-4 nm in diameter in amorphous CNFs. TEM observation revealed that the local graphitization started to occur at annealing temperature of 180°C, which is much lower than the graphitization temperature for bulky Sn. The decrease in the melting point for the nano-sized particles was thought to be responsible for the local graphitization at lower temperature.

For the detailed observation of the graphitization process on insulator substrates by TEM, especially by cross-sectional TEM (X-TEM), the substrate thin enough to transmit the incidence electron should be developed. Here the fabrication of Si oxide nanofiber (SON) formed on a tip of an atomic force microscope (AFM) cantilever was also challenged for the future X-TEM observation of catalyst/graphene/substrate interface. Si-included CNFs (Si-CNFs) were fabricated onto AFM cantilever tips. The prepared Si-CNFs were then annealed at 1000oC in atmospheric ambient to form SON tipped cantilevers. SON, consisting of mostly Si and O, was linear in shape and was amorphous in crystalline structure. The high performance of the SON tipped cantilever was demonstrated for the X-TEM analyses of ZnO films deposited thereon as a test sample, suggesting that it is promising as a substrate for X-TEM analyses.

Thus, this thesis demonstrated the potential of the low-temperature graphene growth for the future device applications.

論文審査結果の要旨

Graphene, a two dimensional allotrope of carbon in a honeycomb lattice, is one of the hottest materials in the nanotechnology and nanoscience fields. Conventionally, it has been synthesized by high temperature processes, such as chemical vapor deposition (CVD) method. So the development of the low-temperature growth is still challenging.

In this thesis, it is successfully demonstrated that the melting point of the catalyst metal plays an important role to achieve the low temperature growth of graphene, based on the high-resolution transmission electron microscopy (TEM) observation of the graphitization process. In order to achieve the low temperature graphene growth, two strategies were attempted for the selection of the catalyst; one is using the low melting point metal as the catalyst and another is using the nano-sized particles to lower the melting point of the metal.

For the first approach, indium (In) was attempted as the catalyst. In order to observe the local graphitization by TEM, In-included carbon nanofibers (In-CNFs) were fabricated on an edge of a carbon foil by Ar^+ ion sputtering of both the carbon foil and an In plate. Depending on the ion energy, graphitization catalyzed by In was observed even for the as-sputtered sample without post annealing. Based on this fact, In and amorphous C films were deposited onto a SiO_2 covered Si substrate, and were then annealed in vacuum at 150 and 200°C. In both cases, clear 2D peak in Raman spectra, which is the evidence of the graphene formation, was observed.

For the second approach, the temperature dependence of catalytic activity in local graphitization for nano-sized catalyst was investigated for CNFs including Sn nanopartilces of 2-4 nm in diameter (Sn-CNFs). TEM observation revealed that the local graphitization started to occur at annealing temperature of 180°C, which is much lower than the graphitization temperature for bulky Sn due to the decrease in the melting point for the nano-sized particles.

For the detailed observation of the graphitization process on insulator substrates by TEM, especially by cross-sectional TEM (X-TEM), the substrate thin enough to transmit the incidence electron should be developed. Towards the future X-TEM observation of catalyst/graphene/substrate interface, the fabrication of Si oxide nanofiber (SON) formed on a tip of an atomic force microscope (AFM) cantilever was also challenged. Si-included CNFs (Si-CNFs) were fabricated onto AFM cantilever tips. The prepared Si-CNFs were then annealed at 1000°C in atmospheric ambient to form SON tipped cantilevers. SON, consisting of mostly Si and O, was linear in shape and was amorphous in crystalline structure. The high performance of the SON tipped cantilever was demonstrated for the X-TEM analyses of ZnO films deposited thereon as a test sample, suggesting that it is promising as a substrate for X-TEM analyses.

Thus, this thesis demonstrated the potential of the low-temperature graphene growth for the future device applications, and is enough worth for PhD thesis.