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学位論文題目	Optimization of graphene growth and its functionalization by chemical vapor deposition （化学気相合成法でのグラフェン成長の最適化と機能化）
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論文内容の要旨

Graphene is one of the hottest materials in nanotechnology due to its particular properties. In order to realize its practical applications, high quality graphene with large domain size to reduce the sheet resistance as well as its band gap engineering should be achieved. In this thesis, these subjects are tackled with graphene synthesized by chemical vapor deposition (CVD) methods on transition metal substrates with several solid precursors.

Chapter 1 describes the motivation and the purpose together with the structure of graphene and the following properties, the different synthesis methods used in the fabrication of graphene, the transfer techniques, the characterizations and current states of the art about graphene research.

Chapter 2 gives details about the CVD method, especially its specific parameters and the used precursors and substrates. The mechanisms on Cu, Ni and CuNi substrates are explained, as well as the design of experiments model with its calculations and optimization process.

Chapter 3 explores the effects of 6 parameters inside the CVD system through two designs of experiments. 2^{5-2} matrixes are used for the study of the parameters with interactions. If the growth temperature has an important effect on the size of crystals, the mass of the carbon source reaches an optimum. The growth time and the pyrolysis rate of the carbon source precursor are the main factor where variations could dramatically change the size of crystals.

Chapter 4 discusses the effect of the pyrolysis rate of the carbon source precursor on the synthesis of graphene on Cu substrate. The continuous carbon supply forms well-defined edges while an abrupt stop of this supply let appear unsaturated edges and nanoribbons at the growth front of the crystals. Monolayer crystals are observed at a low pyrolysis rate of 1.5°C/min, confirmed by Raman spectroscopy. A high pyrolysis rate of 3°C/min generates a small adlayer on the top of the flakes. The graphene crystals grow and finally merge together in a continuous film for a long duration.

Chapter 5 focuses on the functionalization of graphene by the incorporation of nitrogen atoms in the graphitic network. The high carbon and nitrogen solubilities in Ni and the controllability of the synthesis on Cu led to the use of CuNi binary alloy where nitrogen-doped bilayer graphene was synthesized. The use of melamine as the sole precursor of both C and N atoms allowed a 5.8 at % of nitrogen inside the carbon network, confirmed by X-ray photoelectron spectroscopy (XPS).

Chapter 6 investigates the anisotropic etching of graphene by H_2 after the synthesis of graphene flakes and films with camphor. This reverse reaction of graphene growth forms holes in the continuous graphene film, along with symmetric directions of the graphene lattice. A longer duration, nanoribbons with non-uniformed width are created between larger domains. The fabrication of a Y-shaped junction is also observed.

Chapter 7 summarizes this work and explores future prospects.

論文審査結果の要旨

The two dimensional nanocarbon, graphene, is one of the hottest materials in nanotechnology. In order to realize its practical applications, high quality graphene with large domain size to reduce the sheet resistance as well as its band gap engineering should be achieved. In this thesis, these subjects are dealt with for graphene synthesized by chemical vapor deposition (CVD) methods on transition metal substrates with several solid precursors. For the former, for the optimization of the growth parameters, the method of so-called "design of experiment" was applied for the first time. For the latter, two novel approaches for nanoribbon formation and nitrogen doping into bilayer graphene with high nitrogen concentration were tackled.

The numerous parameters inside the CVD system were investigated to increase the size of graphene crystals and control their growth, from the nucleation to the termination at the edges. Designs of experiments for the graphene growth on a Cu substrate using waste plastic as a solid source showed the positive influence of a high temperature on the substrate, while optimums can be found for the mass of the precursor. Remarkably, the change of only the growth time and the pyrolysis rate showed a dramatically change in the graphene domain size. The manipulation of only the pyrolysis rate of the precursor from 1.5 to 3°C/min could tune the carbon supply, which affected the number of layers, synthesizing monolayer and bilayer graphene, respectively. An abrupt stop in the carbon supply led to the formation of unsaturared edges with the presence of nanoribbons, whereas the continuous carbon supply generated well-defined edges.

The need for a band gap in graphene requires the modification of its structure by functionalization. Nanoribbons and other specific structures were formed by H_2 anisotropic etching of graphene after the CVD growth with camphor as a solid carbon source on Cu substrate. The creation of hexagonal holes in graphene and the study of etching demonstrated clearly etching as the reverse process of growth of graphene. The formation of Y-junction nanoribbons with a 120° angle is believed to be particularly interesting in nanoelectronic devices and spintronic applications.

Another possibility for opening a band gap, nitrogen doping into bilayer graphene, was also tackled based on a novel strategy to achieve higher doping concentration. Cu substrate, which is commonly used for monolayer graphene growth, possesses low C and N solubilities, while Ni possesses higher solubilities of these elements. Although due to these higher solubilities, controllability of the number of layer is low for Ni substrate, CuNi binary alloy would possess the suitable controllability of both N doping concentration and the number of layers. Based on this idea, N-doped bilayer graphene growth was challenged using melamine as a sole precursor for C and N atoms. This facilitated the integration of N atoms in the graphitic network, and an incorporation of N as high as 5.8 at% was achieved for a 18°-twisted bilayer graphene.

These new findings provide the basis for various applications, and were published in 4 high-impact factor journals (4 first author papers) including RSC Advances and Applied Physics Letters, and this is enough worth for PhD thesis.