アイハン　ムハッメド　エムレ
氏　名　AYHAN MUHAMMED EMRE

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学位論文題目　Synthesis of Graphene by Chemical Vapor Deposition and Solid Phase Reaction Process towards Next Generation Energy Device Applications
（化学気相法および固相反応法による次世代エネルギーデバイス用グラフェンの合成）
論文審査委員　主査　教授　種村　眞幸
　　　　　　　　　　教授　曾我　哲夫
　　　　　　　　　　教授　日原　岳彦

論文内容の要旨

Two dimensional (2D) graphene crystal is considered to be the main building block of sp^2 hybridized carbon nanomaterials. Due to its unique properties, such as the zero band gap semiconductor, high carrier mobility, optical transparency independent of wavelength, and excellent mechanical strength, graphene is a promising candidate for the nanotechnology and energy-related fields. In this thesis, novel approaches for the synthesis of high quality graphene for the next generation energy device applications are dealt with.

Chapter 1 is the Introduction about synthesis of graphene by chemical vapor deposition (CVD), solid phase reaction approaches and its applications. Motivation of work has also discussed in this chapter.

Chapter 2 is the literature survey. Classification of frontier carbonaceous materials and graphene synthesis methods are presented.

Chapter 3 describes the experimental set-up. Thermal chemical vapor deposition, pulsed laser deposition (PLD) process facilities and characterization facilities such as Raman spectroscopy, SEM, TEM, and AFM are explained.

Chapter 4 deals with the synthesis of graphene on Ag foil by the CVD process as a tarnish-resistant coating was demonstrated. Continuous graphene film on Ag foil was grown using the solid camphor as a carbon precursor with a gas mixture of Ar (85 sccm) and H_2 (5 sccm). The Raman spectroscopy and TEM studies revealed few-layer graphene formation on Ag surface. Tarnishing of the Ag surface in presence of sulfur vapor was investigated with and without coating the graphene film. It was found that the bare Ag surface immediately react with sulfur vapor to turn black, while, graphene-coated Ag surface restrained reacting with the sulfur vapor and thereby preserving the Ag surface. Our findings showed for the first time that graphene film can be effectively synthesized on Ag substrate to resist tarnishing with sulfidation.

Chapter 5 describes a new simple one-step approach to obtain graphene decorated with Ag nanoparticles (Ag-NPs) and their integration for Schottky junction fabrication. Ag-NPs of the size 20-100 nm were directly obtained in the CVD-grown graphene surface by dissolving the base Ag foil of as-synthesized graphene in a diluted HNO_3 solution. The Ag nanoparticles decorated graphene was transferred on an n-Si substrate to fabricate a Schottky junction. Significant photoresponse has obtained with illumination of 3.6, 5.1 and 2.1mW/cm^2 of near-IR (1000 nm), visible (550 nm) and near-UV (350 nm) light, respectively. The Ag-NPs decorated graphene-Si Schottky junction showed photoresponse of 122, 98 and 78mAW^{-1} at 550, 350 and 1000 nm, respectively. The strong photoresponce is attributed to light interaction with the plasmonic Ag-NPs and efficient Schottky junction formation. In the demonstrated device plasmonic Ag-NPs can enhance light absorption and thereby enabling detection of the faintest incident light for a broad-wavelength range.

Chapter 6 demonstrates the successful synthesis of monolayer graphene by a solid phase reaction approach using the triblock co-polymer Pluronic F127 as carbon source. The amount of Pluronic F127 used for thin film deposition by spin coating significantly affects the graphene growth process. We demonstrated that the number of layers can be controlled by optimizing the thickness of the polymer film, annealing duration and the amount of H_2 gas. Thus, the monolayer graphene, which is usually not obtained so easily by solid phase reaction, were synthesized directly on the SiO_2/Si substrate by graphitizing the polymer in presence of the Ni and NiO catalytic and carbon diffusion barrier layer, respectively.

Chapter 7 summarizes the above described results to establish the conclusion.

論文審査結果の要旨

Graphene is one of the most promising candidates for renewable energy device applications, due to the extraordinary electronic, mechanical, optical and chemical properties. However, there are still several obstacles to be solved, including the low light absorption and photoresponsivity in monolayer graphene and transfer process of graphene onto the device. In this dissertation, novel approaches for the synthesis of high quality graphene for the next generation photodetector applications are dealt with.

Chapter 1 is the Introduction about current energy trends and the integration of graphene with next generation energy device applications. Motivation of the work is also discussed in this chapter.

Chapter 2 presents the classification of frontier carbonaceous materials.

Chapter 3 describes experimental set-up including chemical vapor deposition (CVD) system and solid phase reaction system, together with the characterization facilities.

Chapter 4 deals with the synthesis of continuous graphene film on noncatalytic Ag foil by the CVD process using solid camphor as a carbon precursor. The synthesis is achieved for the first time. The Raman spectroscopy and transmission electron microscopy (TEM) studies revealed few-layer graphene formation on Ag surface. Tarnishing of the Ag surface in presence of sulfur vapor was investigated with and without coating the graphene film. It was shown for the first time that the bare Ag surface immediately react with sulfur vapor to turn black, while graphene-coated Ag surface restrained reacting with the sulfur vapor and thereby preserving the Ag surface.

Chapter 5 describes a new simple one-step approach to obtain graphene decorated with Ag nanoparticles (Ag-NPs) 20-100 nm in size and their integration for Schottky junction fabrication. The Ag-NPs decorated graphene-Si Schottky junction showed photoresponse of 122, 98 and 78mAW^{-1} at 550, 350 and 1000 nm, respectively. The strong photoresponce is attributed to light interaction with the plasmonic Ag-NPs and efficient Schottky junction formation. In the demonstrated device, plasmonic Ag-NPs can enhance light absorption and thereby enabling detection of the faintest incident light for a broad-wavelength range.

Chapter 6 demonstrates the successful synthesis of graphene film by a solid phase reaction approach using the triblock co-polymer Pluronic F127 as carbon source. The number of layers can be controlled readily by optimizing the thickness of the polymer film, annealing duration and the amount of H_2 gas. Thus, the monolayer graphene were obtained directly on the SiO_2/Si substrate by graphitizing the tri-block co-polymer in presence of the Ni and NiO catalytic and carbon diffusion barrier layer, for the first time.

Chapter 7 summarizes the above described results to establish the conclusion.

These new findings were published in 3 high-impact factor journals (3 first author papers) including RSC Advance, and this is enough worth for PhD thesis.