

シンデ サチン マルティ

氏名	SHINDE SACHIN MARUTI
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論文審査委員	主査 教授 種村 眞幸 教授 市川 洋 准教授 Kalita Golap

## 論文内容の要旨

Two dimensional (2D) materials such as graphene and transition metal dichalcogenides (TMDCs) monolayer possess unique physical and chemical properties. Graphene is a zero bandgap semiconductor, while TMDCs such as Molybdenum Disulfide ( $\text{MoS}_2$ ) possess a direct band gap ( $\sim 1.8$  eV). Hence, it is quite fascinating to combine these two materials taking advantages of their individual properties to develop novel device applications. In this regards, high quality synthesis and damage free transfer of these materials are two key subjects for practical applications. In this thesis, the synthesis processes of high quality graphene and  $\text{MoS}_2$  layers are explored as well as their clean and damage free transfer onto arbitrary substrate for device fabrications.

Chapter 1 describes mainly the general introduction of 2D materials with their physical and chemical properties together with methods of synthesis. It also includes their effective transfer onto arbitrary substrates. Doping in graphene and graphene based heterostructures are also explained in this chapter.

Chapter 2 deals with the experimental details. Atmospheric chemical vapor deposition (APCVD) technique was employed for the synthesis of 2D materials. Transfer methods for graphene, CNTs

and MoS<sub>2</sub> are also discussed. Nitrogen doping in graphene using different precursors is also a part of this chapter. Details about the fabrication of hybrid structures of graphene with CNTs and MoS<sub>2</sub> are given in this chapter.

In Chapter 3, it is demonstrated that the transfer process of large-area graphene film onto flexible cellulose acetate (CA) substrates by a hot press technique. The CA based substrate was not compatible with acetone and PMMA supporting layer in a conventional transfer process. The CA substrate was hot pressed onto the graphene synthesized Cu foil followed by etching of the base Cu to obtain the graphene coating directly on the CA substrate. A clean, continuous and damage-free graphene transferred onto the CA substrate was obtained. The graphene film on CA substrate is highly conducting ( $R_s \sim 2 \text{ k}\Omega/\square$ ) as measured by electrical measurements, suggesting that it can be used as building block for paper based electronic devices. The developed process can be significant for graphene transfer onto moldable substrate materials with the advantage of not using polymer and organic solvents.

Chapter 4 demonstrates the synthesis process of a three dimensional (3D) hybrid structure of Graphene and vertically aligned multi-wall CNTs (VAMWCNTs) using a single solid carbon source (camphor). Optical and transmission electron microscopies (TEM) confirmed the out-of-the plane growth of the CNTs on the transferred graphene film and structure of CNTs and graphene in the 3D system. Current-voltage (I-V) measurements were carried out to investigate in plane and out of plane electrical characteristics of the 3D system. The VAMWCNTs-graphene structure showed a contact resistance of  $255\Omega$  and this low contact resistance can be significant for practical device applications.

In chapter 5, Graphene-MoS<sub>2</sub> heterostructure and its application in non-volatile memory device have been discussed. TEM and scanning transmission electron microscopy - high-angle annular dark-field (STEM-HAADF) studies were carried out to observe the atomic level structure of the synthesized high quality MoS<sub>2</sub> crystals. An on/off ratio as high as  $2.5 \times 10^3$  was obtained in the fabricated Polymethyl methacrylate (PMMA)-MoS<sub>2</sub>/graphene memory device which is attributed by charge trapping and de-trapping behavior of MoS<sub>2</sub> in the presence of PMMA. The developed material system and the demonstrated memory device fabrication process can be a significant platform for next generation data storage applications.

In Chapter 6, N-doped graphene synthesis using Melamine, Polyacrylonitrile (PAN) and 1,3- triazine as a N-source and Camphor as a C-source, respectively, by APCVD technique is explained. The atomic percent of nitrogen was tuned by varying the amount of precursors. Raman and x-ray photoelectron spectroscopy (XPS) analysis was carried out to confirm the presence and amount of nitrogen in given samples. Melamine with camphor was turned out to be the best choice among above precursors since it provide 5.2 at % of N which is highest among them

Chapter 7 summarizes the whole thesis and future prospects.

## 論文審査結果の要旨

Low dimensional nanomaterials such as carbon nanotubes (CNTs), graphene and molybdenum disulfide ( $\text{MoS}_2$ ) monolayer, a kind of transition metal dichalcogenides (TMDCs), possess unique physical and chemical properties. Hence, it is quite fascinating to hybridize those nanomaterials taking advantages of their individual properties to develop novel device applications. In this thesis, the synthesis, transfer and hybridization of those nanomaterials are tackled.

Chapter 1 describes a brief introduction about graphene, N-doped graphene,  $\text{MoS}_2$  and CNTs.

Chapter 2 deals with all instrumental methods including synthesis of pure and N-doped graphene,  $\text{MoS}_2$ , and vertically aligned CNTs, together with the transfer methods for graphene and  $\text{MoS}_2$ .

Chapter 3 demonstrates the transfer process of large-area graphene film onto flexible cellulose acetate (CA) substrates by a hot press technique. Using this technique, clean, continuous and damage-free graphene transferred onto the CA substrate was achieved. The graphene film on CA substrate is highly conducting ( $R_s \sim 2 \text{ k}\Omega/\square$ ) as measured by electrical measurements. The developed process can be significant for graphene transfer on various moldable substrate materials.

In Chapter 4, the synthesis process of a three dimensional hybrid structure of graphene and vertically aligned CNTs using a single solid carbon source (camphor) is demonstrated. Highly dense vertically aligned CNTs were grown on a transferred graphene film to fabricate the hybrid structure. The achieved seamless contact of vertically aligned CNTs - graphene film is significant for low contact resistance ( $255\Omega$ ) and thereby practical device application.

In chapter 5, graphene- $\text{MoS}_2$  heterostructure and its application in non-volatile memory device have been discussed. An on/off ratio as high as  $2.5 \times 10^3$  was obtained in the fabricated polymethyl methacrylate (PMMA)- $\text{MoS}_2$ /graphene memory device which is attributed by charge trapping and de-trapping behavior of  $\text{MoS}_2$  in the presence of PMMA. The developed material system and the demonstrated memory device fabrication process can be a significant platform for next generation data storage applications.

Chapter 6 deals with the N-doped graphene synthesis using melamine, polyacrylonitrile (PAN) and 1, 3- triazine as a N-source and camphor as a C-source, respectively, by atmospheric chemical vapor deposition technique. Rate and amount of evaporation are the key factors to get good quality of N-doped graphene. As confirmed by Raman and x-ray photoelectron spectroscopy analyses, melamine with camphor was turned out to be the best choice among the precursors tested here since it provided 5.2 at % of N which was highest among them

Chapter 7 summarizes the whole thesis and future prospects.

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