	サラマ　カマル　プラサド
氏　　　名	SHARMA KAMAL PRASAD
学位の種類	博士（工学）
学位記番号	博第1134号
学位授与の日付	平成30年3月30日
学位授与の条件	学位規則第４条第１項該当　課程博士
学位論文題目	Synthesis and characterization of graphene and hexagonal BN crystals on Cu by chemical vapor deposition using solid precursors （固体前駆体を用いた化学気相合成法によるグラフェン及び六方晶BN結晶のCu上への合成と評価）
論文審査委員	主査　教授　種村　眞幸 教授　曾我　哲夫 准教授　Kalita Golap

論文内容の要旨

Among hundreds of layered material investigated till now, graphene (a semimetal) and hexagonal boron nitride (h-BN, an insulator) attracted significant attention due to their promising properties in a wider range of applications. Best synthesis technique is highly desirable for the synthesis of nanomaterials at least with their pristine quality performance. The synthesis of graphene and h-BN by chemical vapor deposition (CVD) has been explored as a most scalable method than other synthesis techniques. However, the issues of crystalline quality in CVD synthesized films should be addressed through the synthesis route of single crystals. In this thesis, this issue is tackled so as to control over the catalytic substrate (Cu) and precursors used.

Chapter 1 is the introduction part about the recent progress of graphene and h-BN, including their synthesis methods, unique properties and potential applications. The motivation and purpose of the thesis are also included in this chapter.

Chapter 2 discusses the materials and methods adopted for the synthesis and characterization of graphene and h-BN. Their growth mechanism in CVD process and the most popular transfer

techniques are summarized. This chapter also emphasizes the CVD system and transfer process along with the detailed characterization process used in the present work.

Chapter 3 deals with the influence of the polycrystalline structure of Cu foil on anisotropic etching for as-synthesized graphene using polystyrene as a solid precursor in a low-pressure CVD system. The etching process can be an ideal reverse phenomenon to recognize graphene growth behavior as well as opening new opportunities to control the graphene structure. Microscopic analysis showed that both the growth and post-grown etching of graphene crystals were significantly affected by the crystallographic nature of Cu grains. The hexagonal hole formation with anisotropic etching was observed to be independent of the stripes and wrinkles in the synthesized graphene. In addition, the variation in etched pattern of the graphene depending on the base Cu grain orientations was observed, attributing to the difference in nucleation and growth processes.

Chapter 4 discusses the annealing process to create an oxide layer and subsequent recrystallization of Cu foil for the growth of large graphene domains using polystyrene as a solid precursor by the atmospheric pressure CVD technique. The electroless polished Cu foils were annealed in Ar and successively in H_2 atmosphere to obtain smoother surfaces with reduced graphene nucleation sites. The transformation of Cu grain structures at various annealing steps was confirmed, where the gas atmosphere and annealing duration had significant influence. Graphene domains with the size larger than 560 μm were obtained on the processed Cu surface. It was revealed that the oxidation and recrystallization process of Cu foil surface significantly influenced the nucleation density, which enabled the growth of larger graphene domains in the developed CVD process.

Chapter 5 explores the synthesis of morphology controlled h-BN crystals by atmospheric pressure CVD using ammonia borane (AB) as a solid precursor. The shape of crystals could be modulated from hexagonal to triangular by controlling the pyrolysis temperature and the supply rate of AB. These phenomena were attributed to a different growth mechanism, namely, the crystal growth limited by either the edge attachment or diffusion of AB, dependent on the concentration of BN radicals in the growth region.

Chapter 6 deals with the edge controlled growth of h-BN crystals by atmospheric pressure CVD. By controlling the supply of borazine gas generated by the decomposition of AB, the edge controlled growth of an h-BN single crystal larger than 25 μm in edge length was achieved on as-purchased Cu foils. It was also demonstrated that the variation in temperature during the growth and cooling processes induced the formation of wrinkles larger than 20 nm due to the thermal straining of the Cu surface and a negative expansion coefficient of h-BN.

Chapter 7 summarizes this work and explores future prospects.

論文審査結果の要旨

Two-dimensional nanomaterials, such as graphene and hexagonal boron nitride (h-BN), have attracted significant attention due to their unique properties promising for a wider range of applications. Thus, the synthesis of graphene and h-BN by chemical vapor deposition (CVD) has been explored as a most scalable method. However, the controllable growth of their single crystals with high quality and larger domain size is still challenging. In the thesis, this issue is tackled so as to control over the catalytic substrate (Cu) and precursors used.

Chapter 1 is the introduction part. The motivation and the purpose of this thesis are described after the survey on the recent progress in graphene and h-BN researches.

Chapter 2 discusses the materials and methods adopted for the CVD synthesis and characterization of graphene and h-BN.

Chapter 3 deals with the influence of the polycrystalline structure of Cu foil on anisotropic etching for as-synthesized graphene using polystyrene as a solid precursor in a low-pressure CVD system. Microscopic analysis revealed that both the growth and post-grown etching of graphene crystals were significantly affected by the crystallographic nature of Cu grains. In addition, the variation in etched pattern of the graphene depending on the base Cu grain orientations was observed, attributing to the difference in nucleation and growth processes.

Chapter 4 discusses the importance of the pre-annealing process of Cu foils for the growth of large graphene domains using polystyrene in an atmospheric pressure CVD (AP-CVD). The electroless polished Cu foils were pre-annealed in Ar and successively in H_2 atmosphere to obtain smoother surfaces with reduced graphene nucleation sites. Thanks to this optimized pre-annealing of Cu foils, graphene domains with the size larger than 0.56 mm were obtained.

Chapter 5 explores the synthesis of morphology controlled h-BN crystals by AP-CVD using ammonia borane (AB) as a solid precursor. The crystal shape could be modulated from hexagonal to triangular by controlling the pyrolysis temperature and the supply rate of AB, due to the different growth mechanism, namely, the crystal growth limited by either the edge attachment or diffusion of AB.

Chapter 6 deals with the edge controlled growth of h-BN crystals by AP-CVD. By controlling the supply of borazine gas generated by the decomposition of AB, the edge controlled growth of an h-BN single crystal larger than 25 μm in edge length was achieved on as-purchased Cu foils.

Chapter 7 summarizes this work and explores future prospects.

These new findings are believed to open up a new door to the synthesis of the high quality graphene and h-BN, and were published in 4 high-impact factor journals (3 first author papers) including CrystEngComm, that is enough worth for PhD thesis.