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学位論文題目	Chemical Vapor Deposition of Tungsten Disulfide (WS_2) Crystals on Graphene and Hexagonal Boron Nitride (h-BN) （グラフェンおよび六方晶窒化ホウ素(h-BN)上への二硫化タングステン(WS_2)結晶の化学気相合成）
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論文内容の要旨

Transition metal dichalcogenides (TMDs), such as WS_2, have great attention due to their bandgap which is suitable for optoelectronics and nano-electronics applications. This thesis deals with the synthesis of large size WS_2 crystal on graphene and hexagonal boron nitride (h-BN) by atmospheric pressure chemical vapor deposition (APCVD) and their characterization.

Chapter 1 describes the general introduction of two dimensional (2D) layered materials including graphene, h-BN and TMDs, with regard to their properties, applications, physical and chemical synthesis methods.

Chapter 2 deals with the experimental details, including APCVD for the synthesis of 2D materials and transfer methods for graphene and h-BN.

Chapter 3 describes the effect of WO_3 precursor and sulfurization process on WS_2 crystals. The quantity of WO_3 precursor spread over SiO_2/Si substrate significantly affected the nucleation density and number of layers for triangular-shaped WS_2 crystals. Larger triangular crystals (~70 μm) were obtained by controlling the amount of WO_3 precursor as nucleation and

growth sites. Pyramid-like few-layers stacked structure of WS_2 crystals were obtained from densely spread WO_3 powder. By controlling the amount of WO_3 precursor and the rate of sulfur introduction in the high temperature chemical vapor deposition (CVD) zone, large WS_2 crystals were synthesized.

Chapter 4 discusses an effective approach to synthesize high quality monolayer WS_2 crystals using tungsten hexachloride (WCl_6) as solid precursor in APCVD process. In this technique, 0.05M solution of WCl_6 in ethanol was drop casted on SiO_2/Si substrate to create a uniform distribution of the precursor, which was reduced and sulfurized at 750 °C in argon atmosphere. The growth of triangular, star-shaped, as well as dendritic WS_2 crystals on the substrate was observed. The crystal geometry evolved with shape and size of the nuclei as observed from the dendritic structures. This finding shows an easier and effective approach to grow WS_2 monolayer crystals using tungsten halide coating on substrate surface rather than evaporating the precursor for gas phase reaction.

In Chapter 5, synthesis of graphene and the effect of hydrogen etching were studied upon graphene crystals and continuous film. Highly anisotropic and fractal etching was demonstrated with the formation of hexagonal graphene hole, ribbon like structures and hexagonal-hexagonal stacking (stacking of three hexagonal layers) along with the snowflake dendritic crystals. This finding can be significant to understand the nucleation and growth of graphene crystals as well as their selective etching process to fabricate well-defined structures.

Chapter 6 discusses the synthesis of WS_2 triangular crystals of 2-7 μm in size using WO_3 and S powder precursors on the CVD grown graphene and h-BN films. On the other hand, the vertically aligned WS_2 sheet formed using densely spread WO_3 powders on SiO_2/Si and graphene substrates.

Chapter 7 summarizes the whole thesis and future prospects.

論文審査結果の要旨

Transition metal dichalcogenides, especially tungsten sulfide (WS_2), have great attention due to their bandgap which is suitable for optoelectronics and nanoelectronics applications. In this work high quality of WS_2 crystals were synthesized using atmospheric pressure chemical vapor deposition (APCVD) technique. Various experimental parameters of the developed chemical vapor deposition (CVD) process were optimized to synthesize large WS_2 monolayer crystals.

Chapter 1 describes mainly the general introduction of two dimensional (2D) materials.

Chapter 2 deals with the experimental details, including APCVD for the synthesis of 2D materials and transfer methods for graphene and h-BN.

In chapter 3, the effect of sulfurization process and quantity of WO_3 precursor on the growth of WS_2 crystals is revealed. Pyramid-like few-layers stacked structure of WS_2 crystals were obtained from densely spread WO_3 powder. Larger triangular crystals (~70 μm) were obtained by reducing the amount of WO_3 precursor. The uniform high-quality monolayer WS_2 single crystals (300 μm) were successfully grown by optimizing the arrangement of the substrate in CVD system.

Chapter 4 deals with a simpler and effective approach to synthesis high quality monolayer WS_2 crystals using drop-casted WCl_6 precursor on SiO_2/Si substrate. The high quality WS_2 crystals grew using 0.05M WCl_6 precursor with well distribution of nucleation sites on the substrate. Depending on the amount of the precursor, various shapes of WS_2 crystals were formed, such as triangular, star-shaped, and dendritic structures of six arm-star-shaped, like a snowflake crystal.

Chapter 5 describes the H_2 induced etching features of graphene crystals of six-lobed dendritic structures along with regular hexagonal structures on electro-polished Cu foils. The etching of all snowflake dendritic crystals occurred from the branches of lobs, creating symmetrical fractal pattern. On the other hand, the regular hexagonal crystals were etched anisotropically to form hexagonal hole and ribbon like structures with pronounced edges. It is believed that these findings should be fundamental to the formation of well-defined graphene structures with controlled edges for the future nano-electronics applications.

In Chapter 6, it is demonstrated that WS_2 triangular crystals of 2-7 μm in size were synthesized using WO_3 and S powder precursors on the CVD grown graphene and h-BN films. On the other hand, the vertically aligned WS_2 sheet formed using densely spread WO_3 powders on SiO_2/Si and graphene substrates.

Chapter 7 summarizes the whole thesis and future prospects.

Above-mentioned new findings will open up a new door to the synthesis of the high quality 2D nanomaterials and were published in three high-impact factor journals such as Applied Physic Letters, that is enough worth for PhD thesis.