

Controlled CVD Growth of High-Quality 2D Materials and Their Heterostructures for Device Applications

Hiroki Ago

Global Innovation Center (GIC) and Interdisciplinary Graduate School of Engineering Sciences
Kyushu University, Kasuga, Fukuoka 816-8580, Japan
Phone: +81-92-583-8852 E-mail: h-ago@gic.kyushu-u.ac.jp

Abstract

Two-dimensional (2D) materials have attracted great interest because of their unique and excellent physical properties which promise electronic and photonic applications. In this talk, I will introduce our recent research on 2D materials, mainly focusing on synthesis of high-quality 2D materials by chemical vapor deposition (CVD) method. The CVD synthesis of transition metal dichalcogenides (TMDCs), graphene, and hexagonal boron nitride (h-BN) are presented. In addition, studies on heterostructures of these 2D materials, both in-plane and stacked heterostructures, are also presented, associated with their electronic and optical properties.

1. Introduction

The development of graphene research has opened a new field of atomically thin, two-dimensional (2D) layered materials. They have unique properties, such as high carrier mobility, mechanical flexibility, optical transparency, high thermal conductivity, and high degree of freedom of stacking angles. These properties stimulate the research on the applications of 2D materials to electronic and photonic devices. However, for realizing such applications, it is very important to synthesize large-area 2D materials with high crystallinity and low defect density. In this presentation, our recent progress of the chemical vapor deposition (CVD) growth of transition metal dichalcogenides (TMDCs), graphene, and hexagonal boron nitride (h-BN) is presented with the emphasis on our original epitaxial growth approach for high-quality films. Moreover, I will also demonstrate our recent work on different types of 2D heterostructures.

2. TMDCs

Recently, TMDCs consisting of transition metal (such as Mo, W, Nb) and chalcogen (S, Se, Te) atoms have attracted great interest. These atomically thin, 2D materials exhibit excellent physical properties, such as high optical quantum yield, layer number-dependent bandgap, and large valley splitting. We grow MoS₂ (and WS₂) by thermal CVD using MoO₃ (WO₃) and S powders as feedstock. By controlling the CVD condition, well-aligned single crystal grains of MoS₂ (and WS₂) were successfully obtained on c-plane sapphire (α -Al₂O₃) substrates [1-3]. As shown in Figure 1a, randomly oriented WS₂ grains are generally obtained by conventional CVD method. We found that introduction of H₂ gas in Ar flow results in the growth of highly aligned WS₂, as

shown in Figure 1b,c [1]. In the case of MoS₂, the precise control of the S supply rate lead to the aligned, epitaxial growth [2]. The observed epitaxial growth is accounted for by the enhanced interaction between MoS₂ (WS₂) and sapphire surface [1-3]. The H₂ flow reduces the sapphire surface making Al-rich surface, which enhances the WS₂-sapphire interaction. Scanning transmission electron microscope (STEM) was used to analyze the grain boundaries in the CVD-growth WS₂. In the misoriented grains, we observed many structural defects, such as 7-5 membered rings, forming along boundaries (GBs) [1]. On the other hand, when we added H₂ gas during the CVD process, almost no structural defects were observed except for linear dislocations (Figure 1d). This grain stitching of the aligned WS₂ grains was found to be more chemically stable than misaligned grains, because the latter was facile to be oxidized along the GBs. Moreover, the transport study indicated that the grain stitching is effective to reduce the electrical resistance originated in the GBs [1].

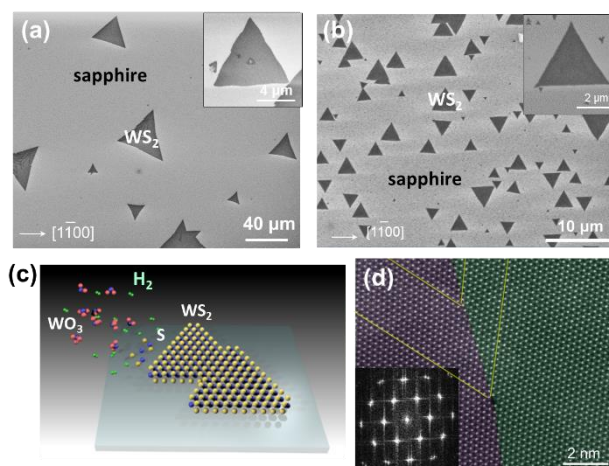


Figure 1 (a) SEM images of randomly oriented (a) and aligned (b) WS₂ grains. (c) Schematic of the epitaxial WS₂ growth on the sapphire. (d) STEM image of the interface between merging two WS₂ grains. Green and purple show neighboring grains, and yellow lines correspond to the dislocations.

With the analogy to modern Si electronics, establishing a method to convert TMDC to p- and n-type semiconductors is essential for various device applications, such as complementary metal-oxide-semiconductor (CMOS) circuits and photovoltaics. However, the control of the polarity in TMDC devices is still difficult, because most of TMDCs, such as MoS₂

and WS₂, are n-type semiconductors and others, WSe₂, show ambipolar behavior. Very recently, we developed a new approach to precisely tune the transport property of WSe₂, changing from ambipolar to p- and n-type transistors in a controlled manner [4]. This finding was further developed to fabrication of CMOS inverter and p-n junction [4]

3. Graphene

Large-area graphene has been widely synthesized on commercial Cu foil, because Cu preferentially gives monolayer graphene due to self-limiting mechanism. We have developed our original epitaxial method which employs a Cu(111) thin film deposited on c-plane sapphire substrate. The highly crystalized Cu(111) film allowed us to control the orientation of hexagonal lattice of monolayer graphene, resulting in the superior graphene performance than other graphene sheets synthesized on Cu foils [5-8]. Wafer-scale CVD production on 4-inch Cu(111)/sapphire was also demonstrated.

Bilayer graphene (BLG) is important because of its tunability of band gap by an external vertical electric field. We have also developed the epitaxial CVD method to selectively synthesize BLG using Cu-Ni(111) alloy film [9]. The unique 2D nanospace sandwiched by two graphene layers were used to intercalate metal chloride, obtaining significant reduction of the sheet resistance [10].

4. h-BN

Since 2D materials, such as graphene and TMDCs, are very sensitive to surroundings due to their atomically thin layered structure with most of the atoms exposed to outside. Therefore, graphene transistors directly made on SiO₂ substrate does not give sufficiently high carrier mobility, because the presence of dangling bonds, surface roughness, and optical phonon, strongly affect carrier transport of graphene on top. The insertion of h-BN to the interface between graphene and SiO₂ significantly increases the graphene's carrier mobility, because h-BN can screen out the influences from the underlying SiO₂ substrate. Moreover, the mobility can be further improved by protecting the graphene top surface by covering with a h-BN layer. Thus, currently, h-BN is essential material for realizing the potential of various 2D materials.

We have also developed epitaxial CVD method to grow monolayer h-BN using Cu(111) and Ni(111) films on sapphire (Figure 2a) [11,12]. When we used Ni(111), very large monolayer h-BN grains with a lateral size of 0.5 mm were successfully obtained, as shown in Figure 2b. This is one of the largest h-BN grains reported so far.

For the application of h-BN to insulating substrate, multilayer h-BN is more favorable, because monolayer h-BN is too thin to screen out influence from the environment. However, the synthesis of uniform and large-area, multilayer h-BN is very difficult so that most of the research works use h-BN flakes exfoliated from bulk h-BN crystal. The size of multilayer h-BN flakes is very small, ~10 μm, thus requiring large-area multilayer h-BN. By optimizing the catalyst,

supporting substrate, and growth condition, we succeeded in obtaining uniform multilayer h-BN with a thickness of 2.5 nm, as shown in Figure 2c,d [13]. We grew monolayer WS₂ grains on the surface of this h-BN film and obtained intense and sharp photoluminescence from WS₂. This result indicates that our CVD-grown h-BN can effectively screen out the influences from SiO₂ surface.

5. Heterostructures

Combination of different types of 2D materials are intriguing. We also show our recent progress of the 2D heterostructure synthesis, such as graphene-MoS₂ (both in-plane and stacked) [2,14,15] and MoS₂-SnS heterostructures [16].

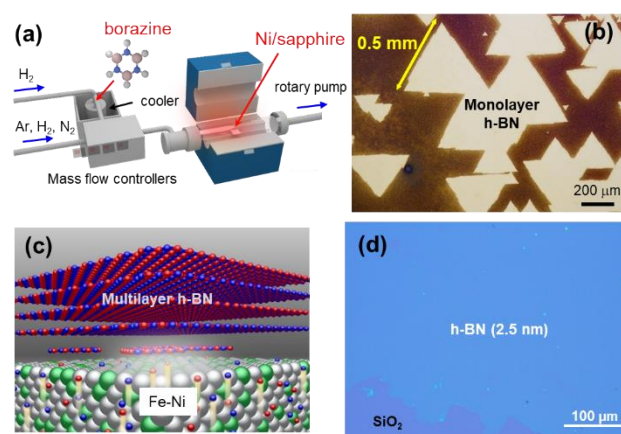


Figure 2 (a) CVD setup used to grow monolayer h-BN. (b) Very large monolayer h-BN grains grown on Ni(111) surface. (c) Schematic of multilayer h-BN growth on Fe-Ni alloy catalyst. (d) Optical micrograph of multilayer h-BN transferred on SiO₂ substrate.

Acknowledgements

This work was supported by JSPS KAKENHI grant numbers JP17K19036 and JP18H03864, and JST CREST grant numbers JPMJCR18I1.

References

- [1] H. G. Ji *et al.*, *Chem. Mater.*, **30**, 403 (2018).
- [2] K. Suenaga *et al.*, *ACS Nano*, **12**, 10032 (2018).
- [3] H. G. Ji *et al.*, *Phys. Chem. Chem. Phys.*, **20**, 29790 (2018).
- [4] H. G. Ji *et al.*, submitted.
- [5] H. Ago *et al.*, *J. Phys. Chem. Lett.*, **3**, 2228 (2012).
- [6] Y. Ogawa *et al.*, *Nanoscale*, **6**, 7288 (2014).
- [7] H. Ago *et al.*, *Chem. Mater.*, **27**, 5377 (2015).
- [8] Y. Miyoshi *et al.*, *Nat. Commun.*, **9**, 1279 (2018).
- [9] Y. Takesaki *et al.*, *Chem. Mater.*, **28**, 4583 (2016).
- [10] H. Kinoshita *et al.*, *Adv. Mater.*, **29**, 1702141 (2017).
- [11] Y. Uchida *et al.*, *Phys. Chem. Chem. Phys.*, **19**, 8230 (2017).
- [12] A. B. Taslim *et al.*, *Nanoscale*, in press.
- [13] Y. Uchida *et al.*, *ACS Nano*, **12**, 6236 (2018).
- [14] A. S. Aji *et al.*, *Adv. Funct. Mater.*, **27**, 1703448 (2017).
- [15] H. Ago *et al.*, *ACS Nano*, **10**, 3233 (2016).
- [16] A. S. Aji *et al.*, *Phys. Chem. Chem. Phys.*, **20**, 889 (2018).