Growth, characterization, and functionalization of graphene and hexagonal boron nitride

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Abstract

Towards electronics/photonics applications of graphene and related two-dimensional materials, we are conducting a wide range of research from their basic physics to device fabrication. In this paper, we review our recent research activities on growth, characterization, and functionalization of graphene and hexagonal boron nitride.

1. Introduction

Graphene, a two-dimensional (2D) sheet of carbon atoms arranged in a honeycomb lattice, is attracting intense attention from fundamental research to technological applications. Graphene has huge potential for applications due to its fascinating electrical, optical, and mechanical properties. The experimental discovery of graphene has also renewed interest in the other two-dimensional materials such as insulating hexagonal boron nitride (h-BN) and semiconducting transition metal dichalcogenides. Their heterostructures are also being actively investigated from the expectation of new physics and new functions. We are conducting a wide range of research on the physics and device applications of graphene and related 2D materials towards their electronics/photonics applications. In this paper, we review our recent research activities on growth, characterization, and functionalization of graphene and h-BN.

2. Isotopic labeling of grain boundaries in graphene

Chemical vapor deposition (CVD) is a scalable, cost-efficient synthesis method of graphene and h-BN. As the substrate for CVD of graphene, polycrystalline Cu foils are normally used. However, graphene grown on polycrystalline substrates is inevitably polycrystalline. The grain boundaries in graphene are known to degrade its electrical and mechanical properties. Therefore, a facile method of visualizing the grain boundaries is desirable. Here, we demonstrate that the grain boundaries are identified using Raman spectroscopy, one of the most standard methods of characterizing graphene, through an isotopic labeling technique.

Isotope labeled graphene was grown by sequential supply of hydrogen and a mixture of ^{13}C methane and hydrogen after standard CVD growth with full coverage of the Cu surface using a mixture of normal methane and hydrogen. ^{12}C-graphene and ^{13}C-graphene are easily discriminated using Raman spectroscopy, because the Raman shift depends on the atomic mass. Figure 1 shows the Raman spectra of the labeled graphene and Raman maps of the G band intensities of ^{12}C-graphene and ^{13}C-graphene. The ^{13}C-G band map shows a network-like structure suggested to be the grain boundaries. To check whether the network-like structure really corresponds to the grain boundaries, we measured the low-energy electron microscopy (LEEM) images and Raman maps at the same areas. Dark-field (DF) LEEM using first-order diffraction spots from graphene can selectively image grains of the same crystal orientation. From the comparison between the DF-LEEM images and Raman maps, we confirmed that the grain boundaries are seen as ^{13}C-rich regions in the Raman maps.

The above results indicate that dynamical exchange of carbon atoms between graphene and the environment happens during the CVD growth of graphene. This facile visualization method of grain boundaries could be useful for investigating the growth mechanism of graphene and their effects on graphene's physical properties.

3. CVD of h-BN on heteroepitaxial Co films [1]

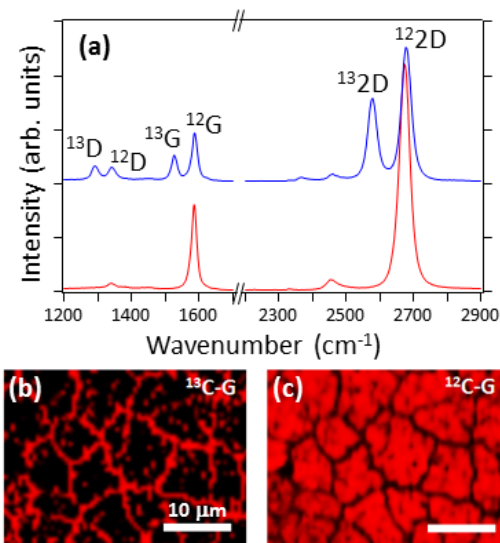One way of eliminating grain boundaries in graphene

Fig 1: (a) Typical Raman spectra of isotope labeled graphene at ^{13}C-rich and ^{13}C-deficient regions. Integrated intensity Raman maps of (c) ^{13}G band (1485-1550cm^{-1}) and (c) ^{12}G band (1550-1650 cm^{-1})

and related 2D materials is to grow them epitaxially on single-crystal substrates. Heteroepitaxial metal films can be prepared in large scale, at low cost, and therefore are suitable as substrates for CVD growth. Here, we show CVD of h-BN on heteroepitaxial Co(0001) films sputtered on sapphire.

h-BN was grown at 1000ºC using ammonia–borane (NH_3–BH_3) as the BN precursor. Figure 2 shows LEEM and cross-sectional transmission electron microscopy (TEM) images of the grown h-BN. The surface is covered with monolayer h-BN uniformly except small patches of bare Co substrate and bilayer h-BN. B and N has negligible solid solubilities in Co, and Co surface loses the catalytic activity when it is covered with h-BN. Therefore, h-BN growth is self-terminated at monolayer.

At the initial stages of h-BN growth, triangular h-BN islands with two opposite directions are formed. Low-energy electron diffraction patterns from the two types of islands have three-fold symmetry and are also reversed with each other. This means that the B-N bond direction is reversed between the two islands. It is known that h-BN on Co has two energetically stable structures [2]. N atoms always sit on top of the first-layer Co atoms, but B atoms can reside on top of the second-layer Co atoms or the hollow sites. Currently our monolayer h-BN always consists of two types of domains, which should cause defects in between. We need further study for single-crystal h-BN growth.

4. Fabrication of graphene pn junction by interface modification [3]

Here, we show that deposition of organosilane self-assembled monolayers (SAM) on the SiO_2 substrate, where graphene is transferred to fabricate field effect transistors (FET), enables us to achieve scalable and reliable p- and n-type graphene and graphene p-n junction. This SAM modification also greatly improves the characteristics of FETs compared to those on the substrate without modification.
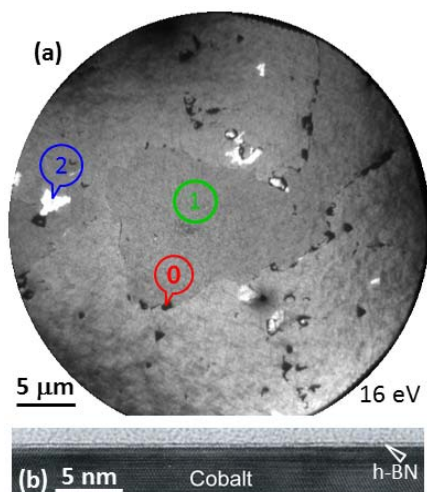

Fig 2: (a) LEEM and (b) cross-sectional TEM images of h-BN grown on a heteroepitaxial Co film by CVD. Numbers in (a) indicates number of h-BN layers.
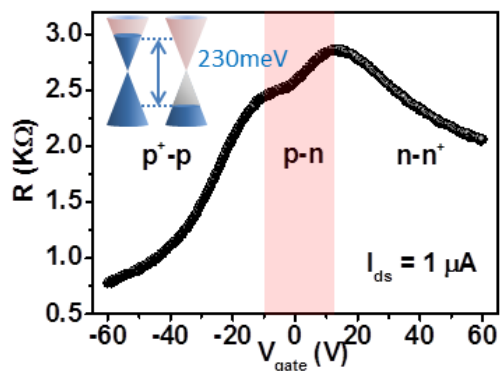

Fig 3: Transfer curve of graphene pn junction FET fabricated through the interface modification using silane SAMs.

Predeposition of silane molecules containing CH_3-group and NH_2-group make the transferred graphene p-type and n-type, respectively. Therefore, lithographically fabricated patterns of CH_3- and NH_2-SAMs can lead to graphene pn junctions. Figure 3 shows the transfer curve of the graphene pn junction FET. The transfer curve contains two peaks corresponding to two Dirac points separated by ~230 meV. We hope that the pn junctions will be useful for investigating the Dirac Fermion physics and fabricating photonic devices like photodetectors.

5. Tunnel device using CVD-grown monolayer h-BN [4]

We fabricated tunnel device of CVD-grown monolayer h-BN sandwiched by Au electrodes and investigated the tunnel barrier properties of h-BN. To determine the tunnel barrier properties correctly, great care is required to remove protective polymer layers used in the transfer process of CVD-grown h-BN. After optimizing the removal procedure, we obtained tunnel barrier height (~2.5 eV) and dielectric strength (~3.78 GVm^{-1}), comparable to those of exfoliated h-BN. CVD-grown h-BN can be an alternative to exfoliated h-BN for tunneling applications, such as vertical transistors and spintronics, with an advantage of being available in large area.

6. Conclusions

We reviewed our research activities on growth, characterization, and functionalization of graphene and h-BN. Now, we are trying to fabricate their heterostructures and are also synthesizing transition metal dichalcogenides. We hope that our research will contribute to realization of electronics/photonics applications of 2D materials.

References

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