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High-Throughput Growth of Hexagonal Boron Nitride Film Using Porous-Structure Isolation Layer

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Abstract

Chemical vapor deposition is considered as the most hopeful method for the synthesis of large-area high-quality hexagonal boron nitride on the substrate of catalytic metal. However, the size the hexagonal boron nitride films are limited to the size of growth chamber, which indicates a lower production efficiency. In this paper, the utilization efficiency of growth chamber is highly improved by alternately stacking multiple pieces of Cu foils and carbon fiber surface felt with porous structure. Uniform and continuous hexagonal boron nitride films are prepared on Cu foils through chemical vapor deposition utilizing ammonia borane as the precursor. This work develops a simple and practicable method for high-throughput preparation of hexagonal boron nitride films, which could contribute to the industrial application of hexagonal boron nitride.

Keywords

Hexagonal Boron Nitride, Chemical Vapor Deposition, Porous Structure Isolation Layer, High Throughput

1. Introduction

Hexagonal boron nitride (h-BN), with a graphene-like crystal structure, is an important two-dimensional material. Due to its unique physical properties, it has potential application values in a multitude of scientific and technological disciplines. For example, as an insulating material with no dangling bond on the

surface, h-BN plays an important role in the following areas such as charge fluctuation [1], gate dielectric [2], passivation layer [3], coulombic interactions [4], contact resistance [5] and atomic tunneling layer [6]. As an insulating material with the band gap of 6 eV, h-BN owns excellent thermal properties and optical properties, which could be applied in the field of heat dissipation [7] and photoelectronic devices [8] [9] [10].

The key to the realization of above applications is controllable synthesis of large-area high-quality h-BN. Chemical vapor deposition (CVD) is considered as the most hopeful method for the synthesis of large-area high-quality h-BN films on the substrate of catalytic metal. Up to now, significant progress have been made in the preparation of h-BN by CVD, especially the synthesis of single-crystal h-BN on the substrates of single-crystal Cu foils or Ni foils with specific crystal structure [11] [12] [13]. However, limited to the size of the growth chamber, the size of the substrates, therefore the area of h-BN films grown on them was only 20 cm × 10 cm which indicates a high production cost of h-BN films and may be an obstacle to the industrial application of h-BN. In recent years, the industrial preparation of graphene films has been vigorously developed, which could be applicable to the industrial production of h-BN films. There are mainly two methods to produce large-area high-quality graphene films at industrial level. One is to continuously growth of graphene through a "roll to roll" CVD system [14]. The other is to improve the utilization efficiency of growth chamber, such as stacking multiple pieces of Cu foils with carbon materials alternately [15] or rolling up a whole piece of Cu foil isolated by carbon materials [16]. However, during the growth of h-BN, the commonly used precursor were solid state instead of gases, whether the methods used for graphene was applicable to high-throughput production of h-BN is not verified.

Here, multiple pieces of Cu foils and fiber surface felt (CFSF) with porous structure were stacked alternately to improve the utilization efficiency of growth chamber. As isolation layers, CFSF prevents Cu foils from sticking together at high temperature, and the porous structure allows the precursor molecules to diffuse onto the surface of the Cu foil. Uniform and continuous h-BN films were prepared on the substrate of Cu foil by CVD utilizing ammonia borane (NH_3BH_3) as the precursor. Results from various characterization techniques indicate the uniformity and continuous of the prepared h-BN films.

2. Experiment Details

2.1. Preparation of Cu-CFSF Spacer Stack

CFSF (20 g/m^2, 250-μm-thick, Suzhou Kangmai New Material Co. LTD., China) is a commercial product with porous structure, with the characteristics of high temperature resistance and air-permeability (**Figure 1(a)** and **Figure 1(b)**). CFSF was annealed at 1080˚C with 20 standard cubic centimeter per minute (sccm) H_2 (99.999%) and 20 sccm Ar (99.999%) at low pressure mode for 10 hours in a 5-cm diameter quartz tube to remove contaminants on the surface.

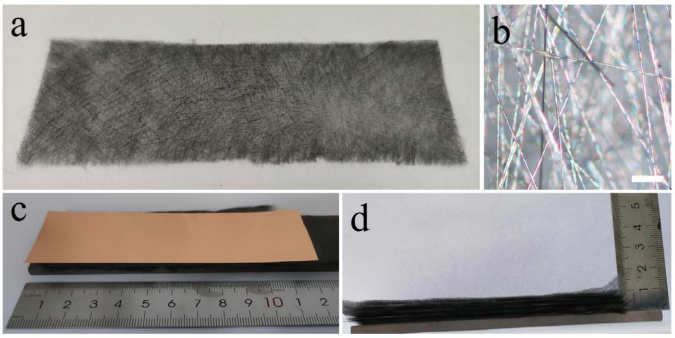

Figure 1. (a) photo of CFSF. (b) OM images of CFSF. The scale is 200 μm. ((c) and (d)) photos of Cu-CFSF stack in the top view and the cross-section view.

Cu foil (50-μm thick, Guantai Metal Materials Co. LTD, China) with the size of 15 cm × 12 cm were electropolished in a solution with a ratio of phosphoric acid to ethylene glycol of 3:1 at 2 V under constant voltage mode for 2 hours to remove contaminants on the surface, followed by rinsed with deionized water several times to clean the residual solution and blown dry with nitrogen. In this paper, CFSF and copper foil were stacked alternately, as shown in **Figure 1(c)** and **Figure 1(d)**. 21 pieces of copper foil and 20 pieces of CFSF were stacked alternately, with a thickness of about 1 cm. It should be noted that the CVD system used in this work was a 5-cm diameter quartz tube double temperature zone CVD system where the length of the constant temperature zone in each single temperature zone is about 10 cm. Therefore, the size of every piece of Cu foil was limited to 4 cm × 12 cm.

2.2. h-BN Growth and Transfer

A home-made CVD system that can be switched between atmospheric pressure CVD (APCVD) mode and low pressure CVD (LPCVD) mode was used for the preparation of h-BN. The Cu-CFSF stack was heated from room temperature to 1050˚C in 40 min and annealed for 30 min with 180 sccm Ar (99.999%) and 20 sccm H_2 (99.999%) under APCVD mode, then the CVD system was switched to LPCVD mode. 30 mg of NH_3BH_3 (Sigma-Aldrich, Product No. 682098, 97%), which was contained in a quartz boat connected to the growth chamber, was heated to 85˚C by heating belt rapped around the quartz tube. The growth of h-BN was lasted for 60 min with 195 sccm Ar (99.999%) and 5 sccm H_2 (99.999%). After the growth of h-BN, the furnace was quickly moved away to cool the samples down to room temperature with the same Ar and H_2 flow. h-BN films were transferred onto 285-nm SiO_2/Si substrate by PMMA-assisted wet transfer technique for further characterizations.

2.3. Characterizations

The Cu foil was heated at 200˚C on a hot plate for 2 min to oxidize the Cu foil for further characterizations. Optical microscopy (Nikon, LV100ND), Raman spectroscopy (Renishaw, Invia Reflex, laser wave length of 532 nm), X-ray pho-

toelectron spectroscopy (XPS, Thermo Scientific K-Alpha) and Electron backscattered diffraction (EBSD, EDAX-TSL) were carried out to analyze the surface morphology, crystal structure and elemental com position of the prepared samples.

3. Results and Discussion

After oxidation, the Cu foils kept their original color, which indicates that the Cu foils were covered with continuous h-BN films, as shown in **Figures 2(a)-(c)**. A control experiment was performed to illustrate the role of CFSF during the growth of h-BN. Under the same growth conditions, with the exception of introducing no NH_3BH_3, Cu foils turned red color when heated at 200˚C on a hot plate for 2 min, indicating that CFSF did not introduce carbon source during the growth of h-BN and merely acted as an isolation layer (**Figures 2(d)-(f)**), which was consistent with previous report [15]. h-BN on the surface of Cu foil were transferred onto SiO_2/Si substrate and characterized by Optical microscopy and Raman spectra. As shown in **Figures 3(a)-(c)**. The h-BN films were continuous and uniform between different layers. The typical Raman spectra of the h-BN in **Figures 3(a)-(c)** exhibited a peak at 1369 cm^{-1} corresponding to the E_{2g} vibration mode of monolayer h-BN as shown in **Figure 3(d)**, which is consistent with previous reports of monolayer h-BN [17]. XPS spectra showed that the binding energies of B 1s and N 1s were located at 190.6 eV and 398.2 eV (**Figures 3(e)-(f)**), respectively, which is consistent with previous report [18]. And element content ratio of B to N was 1:1.04, with the two element of B and N almost equal, indicating that the element of B, N were bonded as B-N, which further demonstrates that the CFSF did not introduce C atom during the growth of h-BN.

Due to the Cu foils used in this work were polycrystalline, and mono-orientation h-BN domains commonly epitaxial growth on the surface of single-crystal Cu foil with specific crystal orientations [11] [12] [17] [18], the prepared h-BN films in this paper were polycrystalline. When the annealing time was extended to 10 hours, the polycrystalline Cu foil was transferred to single-crystal Cu foil with a crystal orientation of (104) (**Figure 4(a)** and **Figure 4(b)**), driven by the

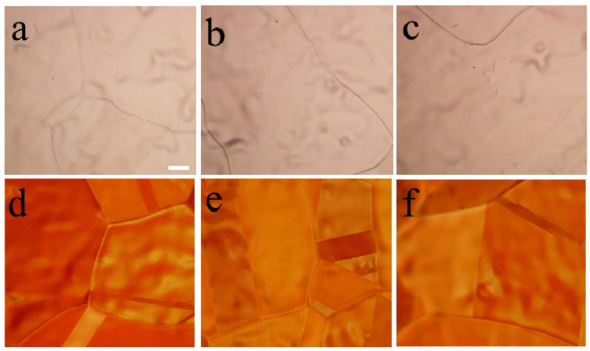

Figure 2. (a)-(c) OM images of the 2nd, 11th, 21th layer Cu foil after h-BN growth and oxidation, respectively. (d)-(f) OM images of the 2nd, 11th, 21th layer Cu foil after CVD growth (without the introduction of NH_3BH_3) and oxidation, respectively. The scale is 20 μm.

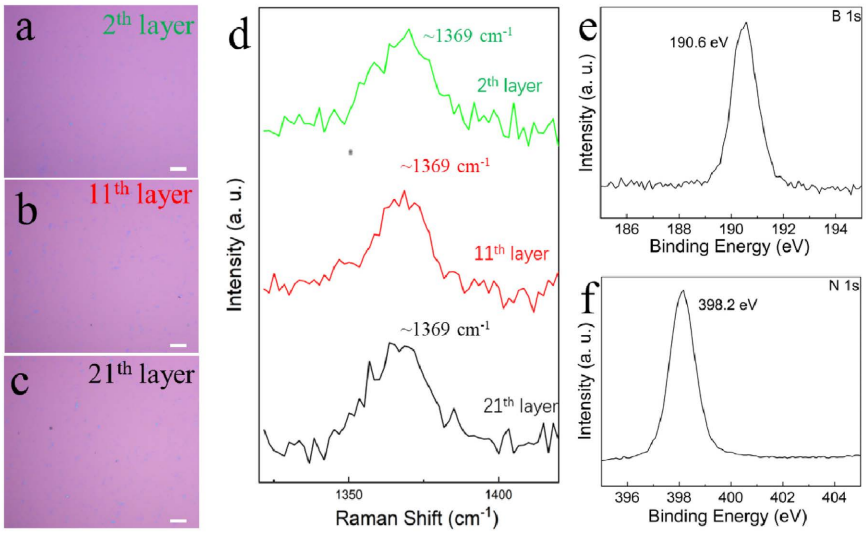

Figure 3. (a)-(c) OM images of the h-BN films grown on the 2th, 11th, 21th layer Cu foil transferred onto SiO_2/Si substrate. The scales are 20 μm. (d) Typical Raman spectra of the samples corresponding to ((a)-(c)), respectively. ((e) and (f)) XPS spectra of h-BN. The binding energies of B 1s and N 1s were located at 190.6 eV and 398.2 eV, respectively.

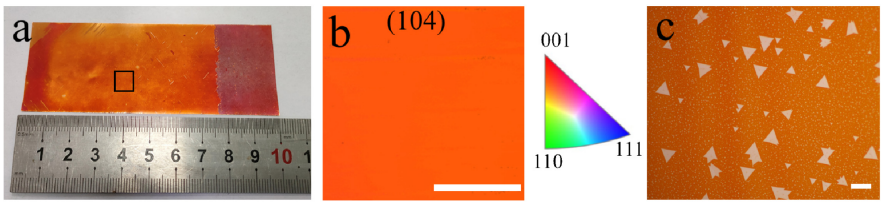

Figure 4. (a) Optical microscopy image of the annealed Cu foil heated at 200˚C on a hot plate for 2 min to oxidize the Cu foil, the left part of the Cu foil was single-crystal Cu foil and the right part remained polycrystalline. (b) EBSD IPF maps of the annealed crystal-crystal Cu marked as black box in (a), with crystal orientations of (104). The Scale is 250 μm. (c) h-BN domains grown on single-crystal Cu foil corresponding to (a) and the Cu foil was oxidized to identify the orientation of h-BN domains. The scale is 20 μm.

stress between Cu foil and CFSF [17]. However, the h-BN domains grown on the annealed single-crystal Cu foil still existed two orientations (**Figure 4(c)**), which could not merge into single-crystal h-BN films. More efforts are needed to prepare single-crystal Cu foils for the synthesis of single-crystal h-BN films.

4. Conclusion

In summary, we have reported a Cu-CFSF stack strategy for high-throughput growth of h-BN films. Uniform and continuous h-BN films on 21 pieces of Cu foils isolated by CFSF are prepared by CVD. This work provides an easy and feasible method for high-throughput growth of h-BN, which may be helpful for the industrial application of h-BN.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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