

# Triggering the atomic layers control of hexagonal boron nitride films



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## ABSTRACT

In this work, we report the successful synthesis of large scale hexagonal boron nitride films with controllable atomic layers. The films are grown on thin nickel foils via ambient pressure chemical vapor deposition with borazine as the precursor. The atomic layers of h-BN films can be controlled in a narrow range by adjusting growth time and the cooling rates. Transmission electron microscope results shows the h-BN films exhibit high uniformity and good crystalline. X-ray photoelectron spectroscopy shows the B/N elemental ratio is about 1.01. The h-BN films exhibit a pronounced deep ultraviolet absorption at 203.0 nm with a large optical band gap of  $6.02 \pm 0.03$  eV. The results suggest potential applications of h-BN films in deep ultraviolet and dielectric materials. Growth mechanisms of h-BN films with thickness control are discussed, especially when the synthesized h-BN films after a higher cooling rate show an in-plane rotation angle between bilayers. Both epitaxial growth and diffusion-segregation process are involved in the synthesis of bilayer h-BN films.

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## 1. Introduction

The great progress in graphene based materials has attracted extreme attentions from researchers to two-dimensional materials [1–4]. As an analogue to graphene in lattice structure, h-BN film, has been proved to be a promising substrate for graphene [5–8]. The h-BN film has a wide range of attractive properties, including high temperature stability, high thermal conductivity, high corrosion resistance [9,10], a low dielectric constant [11], absorbance and photoluminescence at deep ultraviolet (DUV) area [12–14]. The properties lead to a number of potential applications as structural, electronic and optical materials. To meet these applications, h-BN films with atomically thickness are utmost required.

Chemical vapor deposition has been proved to be a promising process for the growth of thin films. Compounds with 1:1 B/N stoichiometry such as hexachloroborazine ( $B_3N_3Cl_6$ ), borazine ( $B_3N_3H_6$ ), and trichloroborazine ( $B_3N_3H_3Cl_3$ ), are usually selected as h-BN precursors. Borazine could be a promising choice for the other two precursors would produce hydrogen chloride, which

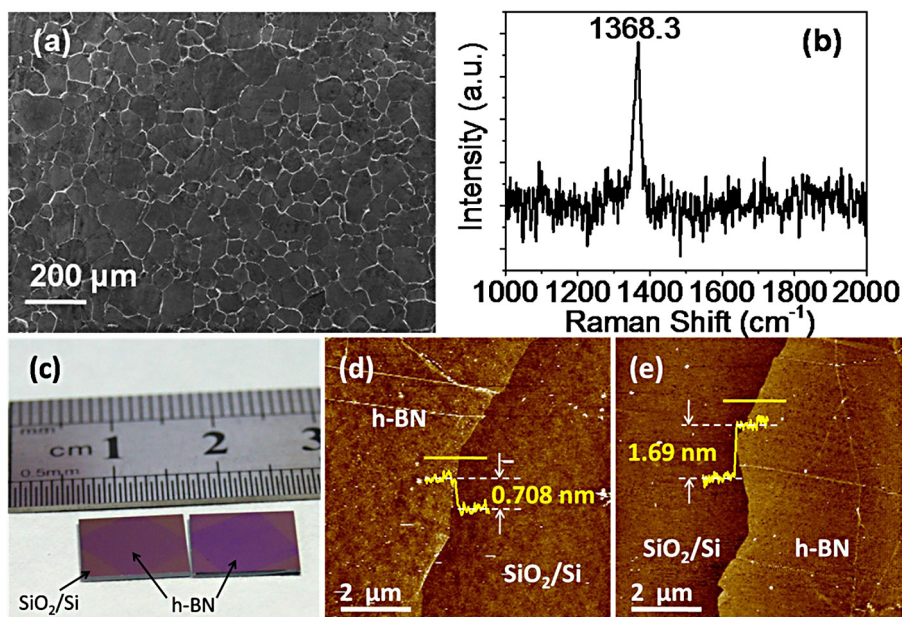
is poisonous and pollutive for environment. CVD synthesis of h-BN films on Ni [15–20], Cu [11,19–23] and other metal substrates [24–28] has been proved, however the authors paid most attention to the synthesis, structure and properties of h-BN films, without giving enough advice on the growth mechanism of h-BN films. The segregation of B and N atoms was discovered during the heat treatment of B and N doped metals [29,30], and has been applied for the growth of h-BN [31–34]. However, before the growth of h-BN, B and N sources usually should be first introduced to the metals by electron beam evaporation or magnetron sputtering, with the employment of extra special instrument. The synthesis of h-BN films with thickness control up to tens of nanometers via CVD has been reported [11,18], without paying much attention to the thickness control for several atomic layers of h-BN. Additionally, substrates have great influence on the h-BN film growth, according to recent reports [19,20], h-BN films grown on Ni tend to show more regular stacking and better crystalline than h-BN films grown on Co or Cu. In order to synthesize h-BN films with atomically thickness and excellent crystalline for the applications in protective coatings, deep ultraviolet emitters and nanoelectronics devices, the growth mechanism and atomic layers control of h-BN films on Ni substrate is studied in this work.

Here we report, the synthesis of high quality large scale h-BN films with thickness control of atomic layers on Ni substrate with borazine as the precursor, using ambient pressure CVD. High

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**Fig. 1.** (a) SEM image of h-BN film grown on Ni foil. (b) Raman spectrum of h-BN films, with the peak at  $1368.3 \text{ cm}^{-1}$  indicating the  $E_{2g}$  vibration mode of h-BN. (c) Photograph of h-BN films on  $\text{SiO}_2/\text{Si}$  substrates with different thickness. (d and e) Typical AFM images of the h-BN films on  $\text{SiO}_2/\text{Si}$  substrates.

purity thin Ni foils are employed and pretreated before the growth of atomically thin h-BN films. The CVD parameters especially the growth time and cooling rates help to control the thickness of the h-BN films. h-BN films show epitaxial growth during CVD, meanwhile the B and N atoms dissolve in the Ni substrate or the grain boundary. Subsequently, during the cooling stage, the B and N atoms exhibit segregation growth of h-BN films.

## 2. Materials and methods

### 2.1. Synthesis of h-BN films

h-BN films were grown on Ni substrate in a alumina tube with a diameter of 50 mm. Ni foils (99.99%,  $25 \mu\text{m}$  thickness, Alfa Aesar) were treated by mechanical and electrochemical polishing. The h-BN precursor borazine was synthesized by the reaction of  $\text{NaBH}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  and purified according to our previous reports [35,36]. With the tube heated to  $1400^\circ\text{C}$  at ambient pressure, the Ni foil was then annealed for 60 min in an argon/hydrogen ( $\text{Ar}/\text{H}_2$ , 5:1, both 99.999% from Pujiang, China) flow of 270 sccm (standard cubic centimeters per minute). After that, the tube was cooled down to  $1000^\circ\text{C}$  slowly for the growth of h-BN. Then, during the growth of h-BN, borazine in a homemade bubbler was introduced to the growth chamber by Ar flow of 2 sccm, while the  $\text{Ar}/\text{H}_2$  flow remained unchanged. The typical CVD growth time was 15–60 min. After the growth, the tube was cooled down to room temperature following various cooling programs.

### 2.2. Transfer and characterizations of h-BN films

The h-BN films were transferred to arbitrary substrates for further characterization by following a typical transfer procedure. Spin-coating thin poly methyl methacrylate (PMMA) film onto the surface of h-BN/Ni, etching the underlying Ni to release the flexible PMMA/h-BN film into diluted HCl and  $\text{FeCl}_3$  ( $\sim 0.5 \text{ mol L}^{-1}$ ) aqueous solution, putting the PMMA/h-BN film onto target substrates, and dissolving the thin PMMA film by acetone. Both images and selected area electron diffraction (SAED) of the h-BN films are obtained in field emission high-resolution transmission electron microscope

(HRTEM, FEI Tecnai  $G^2$  20). Scanning electron microscopy (SEM, Zeiss Supra 55) was employed to show the morphology of h-BN films on Ni foil. X-ray photoelectron spectrum (XPS) was conducted in AXIS Ultra<sup>LD</sup> to analysis the chemical composition of the films. Raman spectroscopy was performed in Thermo DXR with 532 nm laser excitation. UV–visible absorption was measured on h-BN films transferred onto quartz plates in Thermo UV300.

## 3. Results and discussion

### 3.1. Morphology, optical performance, and chemical structure of h-BN films

SEM and Raman spectrum provide useful information for the morphology and lattice vibration modes of h-BN film. Fig. 1 shows the SEM image and Raman spectrum of Ni foil after the deposition of h-BN film. The Raman peak centered at  $1368.3 \text{ cm}^{-1}$  was observed from Ni foil, a result in agreement with the reported values of h-BN [7,12,15,17–21], indicating the existence of h-BN on Ni foil. Moreover, h-BN films on Ni foil were transferred to  $\text{SiO}_2/\text{Si}$  substrates for AFM characterization. AFM results in Fig. 1(c–e) exhibit the morphology as well as the thickness of the h-BN films. As shown in Fig. 1(c), the h-BN films can be observed for the slightly optical contrast between the films and the  $\text{SiO}_2/\text{Si}$  substrates. However, the thicker h-BN film on the right tends to show more intense color contrast than the thinner h-BN film on the left. Fig. 1(d) and (e) shows the h-BN films are with the thickness of 0.708 and 1.69 nm, respectively. These values are very near but slightly higher than the thickness of bi-layer (0.66 nm) and 5 layers (1.65 nm) of h-BN films, which may result from the inevitable contamination during the typical transfer process of h-BN films.

Ultraviolet–visible (UV–vis) absorption spectrum in Fig. 2(a) are measured for the h-BN film with thickness of two layers (0.66 nm) after transferred onto a quartz substrate. The light absorption of the synthesized h-BN film is collected within a wide wavelength range, from 190 to 800 nm.

The synthesized h-BN film exhibits good light transmittance within the above wavelength range, except for a sharp absorption peak at 203.0 nm. As shown in Fig. 2(b), the optical band gap

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