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1 Synthesis of hexagonal boron nitride films by dual temperature zone

2 low-pressure chemical vapor deposition

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15 **Abstract:** In this study, hexagonal boron nitride (h-BN) films were synthesized by dual
16 temperature zone low-pressure chemical vapor deposition (LPCVD) using a single ammonia
17 borane precursor on a non-catalytic c-plane Al_2O_3 substrate. The grown films were confirmed by
18 various characterization methods for h-BN. Meanwhile, the growth rate and crystal quality of
19 h-BN films at different positions in the dual temperature zone were studied. This study found that
20 the growth rate and crystal quality of the h-BN films at different positions on the substrate were
21 significantly different. The growth rate of the h-BN thin films showed a decreasing trend with the
22 rearward position, while the crystal quality improved. This work provides an experimental basis
23 for the preparation of large area wafer thick h-BN films by LPCVD.

24 **Keywords:** Ammonia borane, Dehydrogenation, h-BN, Dual temperature zone

25 **PACS**：61.50.-f, 81.15.Gh, 71.20.Nr,

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1. Introduction

Hexagonal boron nitride(h-BN), SiC and diamond [1-2] are representatives of the third generation of wide-bandgap semiconductor materials. h-BN is a white crystal, and its crystal structure is very similar to graphite, so h-BN is also called "white graphite". h -BN has attracted much attention due to its high-temperature resistance, low coefficient of thermal expansion, high thermal conductivity, low dielectric constant, reliable electrical insulation and excellent optical properties [3]. It has important applications in thermal conductivity **错误!未找到引用源。**, high-temperature oxidation-resistant coating [5], photoelectric devices [6], graphene electronic devices [7], nuclear radiation detection [8] and other fields [910].

There have been various methods to synthesize h-BN, such as mechanical exfoliation, liquid-phase exfoliation and chemical vapor deposition [11]. Among them, chemical vapor deposition (CVD) is a technique for large-area film growth with low manufacturing costs. The chemical vapor deposition synthesis of h-BN has also been reported. For example, using Ni [12], Cu [13], Pt [14] or Si/SiO_2 [15] as the substrate, the synthesis is carried out by LPCVD or APCVD.

At present, the growth of h-BN films by CVD is mainly divided into two directions: the first growth direction is the growth of two-dimensional materials (the growth of a single layer or several atomic layers of h-BN films); The second growth direction is thick film growth, which is used to fabricate semiconductor devices.

There are many precursors for the synthesis of h-BN thin films by CVD, such as ammonia (NH_3) and boron trichloride BCl_3 [16], triethyl borane (TEB) and ammonia (NH_3) [17], diborane (B_2H_6) and ammonia (NH_3) [18], urea (CH_4N_2O) and boric acid (H_3BO_3) [19], borazine [20], ammonia borane [21], etc. However, due to the toxicity of BCl_3, TEB, H_3BO_3, B_2H_6, etc., and the flammability of borazine, for this reason, this paper chooses ammonia borane as the precursor to prepare BN thin films.

For applications such as nuclear radiation detection and optoelectronic devices, this requires high-quality large-area and thick h-BN films, which still faces huge challenges. In addition, the temperature has a great influence on the synthesis of thin films by CVD. Growth at low temperatures is limited by chemical reactions, and at high temperatures, growth is limited by decomposition. Therefore, the temperature field is very important for the synthesis of h-BN, and there is still a lack of research on this aspect. In this paper, to solve the above problems, we use solid ammonia borane as the precursor to study the synthesis of h-BN on the surface of the sapphire substrate under low-pressure conditions. The growth of h-BN in the catalytic metal substrate needs to be transferred. Whereas, the direct epitaxial growth of h-BN on non-catalyzed sapphire substrates more efficiently obtains wafer-scale h-BN and overcomes the surface damage and organic contamination that occurs during transfer. The synthesis of h-BN films was carried out in a tube furnace with a dual temperature zone, and the effect of dual temperature zone on the growth rate of the films and the quality of the film crystals was studied. This study will provide an experimental basis for growing large-area high-quality h-BN films.

2. Experimental process

In this study, h-BN films were synthesized by the LPCVD method. As shown in Fig 1(a), the precursor ammonia borane is heated by an independent box furnace, and using Ar as the carrier

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gas, the product of the thermal decomposition of ammonia borane is introduced into a dual temperature zone high-temperature tubular furnace for BN film growth. As shown in Fig. 1(b), five different positions were taken to study the influence of the dual temperature zone on the film growth rate and the film crystal quality. Positions 1 and 5 were located in the center of the two high-temperature zones, respectively.

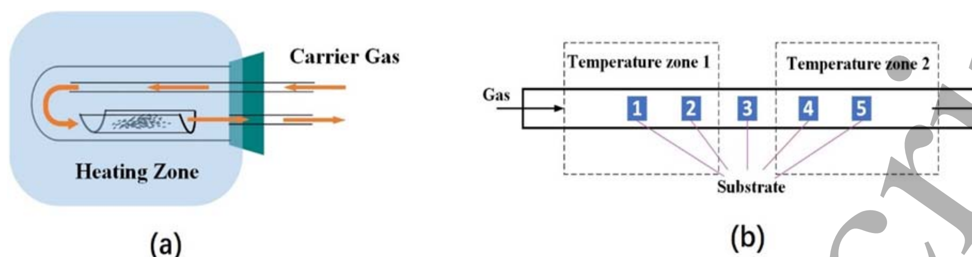

Fig.1 (a) Precursor heating device, (b) Schematic diagram of five substrate positions in the dual temperature zone

The substrate used in the experiment is 1×1 cm^2 c-plane (0001) sapphire (Al_2O_3). First, the five substrates were ultrasonically cleaned with acetone, anhydrous ethanol and deionized water for 10 minutes, and then the substrates were taken out and dried with nitrogen(N_2). Placed in the sample boat and sent to the 5 positions shown in Fig 1(b) respectively, the constant temperature length of the two temperature zones is 290 mm, the distance between each substrate is 80 mm, and the substrate 1 and substrate 5 are located in the center of two temperature zones respectively. Then, the reaction chamber was evacuated to below 1 Pa to remove the air in the tube furnace, and the heating was started through program control and N_2 (80 sccm) was introduced, and the two temperature zones of the tube furnace were heated to 1250 ℃, and after the temperature reached 1250 °C, annealing was performed for 30 minutes to remove oxides on the surface of the substrate. Take 1000 mg of ammonia borane and put it into an independent box furnace (KSL-1100X), start heating, and then heat it to 120 ℃ and use 20 sccm of Ar as the carrier gas to pass the decomposed product of ammonia borane into the tube furnace for growth, and at the same time, N_2 was passed in, and the growth pressure was maintained at 500 Pa. After the growth, the tube furnace temperature was lowered to room temperature under an N_2 gas flow of 50 sccm and the samples were taken out.

The surface morphology and thickness of the h-BN films were characterized by scanning electron microscopy (SEM, Zeiss Merlin Compact). The elemental composition and quantitative analysis of the films were determined by X-ray electron spectroscopy (XPS, Bruker D2 PHASER). The crystal structure and composition of the film were characterized by an X-ray diffractometer (XRD, Thermo Scientific Escalab 250Xi). In this paper, an atomic force microscope (AFM, Bruker Dimension XR) was used to carry out the characterization and analysis of the surface roughness of the h-BN film. In this paper, the transmittance and absorptivity of h-BN films were tested by ultraviolet-visible spectrophotometry (UV-Vis, Agilent Cary 60). In this paper, Raman spectroscopy (Raman spectra, Thermo Scientific DXR2) was used to characterize the material composition and crystal quality of the film. In addition, fourier transform infrared spectroscopy (FTIR) was used in this paper to characterize the chemical bonds present in the sample and the chemical structure of the molecules of the film sample.

3. Results and discussion

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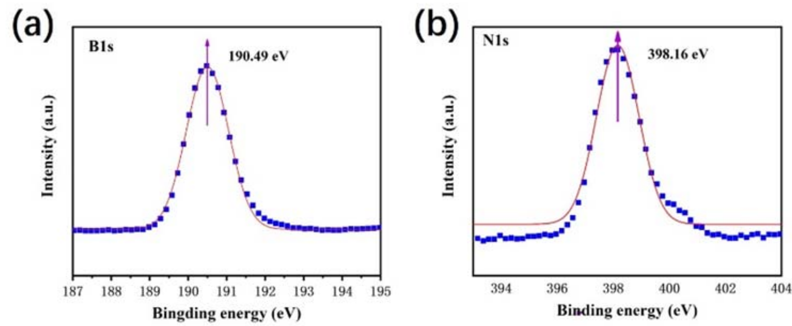

Fig 2 All five samples presented consistent XPS of (a) B1s spectra and (b) N1s spectra.

First, the chemical state of the grown film samples was characterized by XPS, the characterization results of sample 2 are shown in Fig 2(a) and 2(b). The XPS results showed that the binding energies (BE) of B and N were located at 190.49 and 398.16 eV, respectively, corresponding to the B-N bond [22]. This also proves that the synthesized samples are BN films. The degree of dehydrogenation of NH_3-BH_3 is related to the pyrolysis temperature and time, and incomplete dehydrogenation at lower growth temperatures will result in some H atoms remaining to form a small amount of BNH polymer, which shifts the binding energy to the lower energy region. Therefore, the B and N binding energy peaks of the h-BN film samples are slightly lower than the 190.98 eV and 398.78 eV of the single crystal h-BN film.

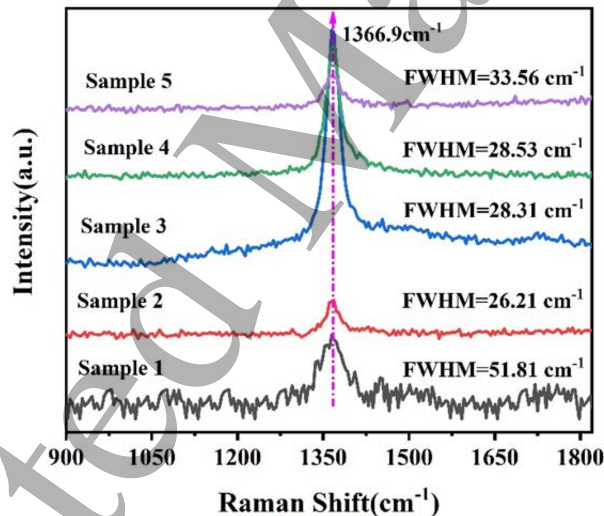

Fig.3 Raman spectra of five samples in the dual temperature zone

Next, the crystalline quality of the h-BN sample films was characterized by Raman scattering spectroscopy. As shown in Fig 3, the five-film samples all have a Raman scattering peak at 1366.9 cm^{-1}, which corresponds to the E_{2g} vibration mode of the B-N bond in the h-BN film, which indicates that the synthesized film is h-BN with hexagonal phase. Compared with the peak of 1365 cm^{-1} for a single crystal h-BN, the peaks of the samples are shifted towards the high-frequency direction, which is caused by the in-plane tensile stress generated by the lattice mismatch between the sapphire substrate and the h-BN film. From the analysis of the FWHM of the five samples, the quality of the other four samples is relatively good except for sample 1. It may be that when the precursor is transported to the No. 1 position, the dehydrogenation is not complete, resulting in a

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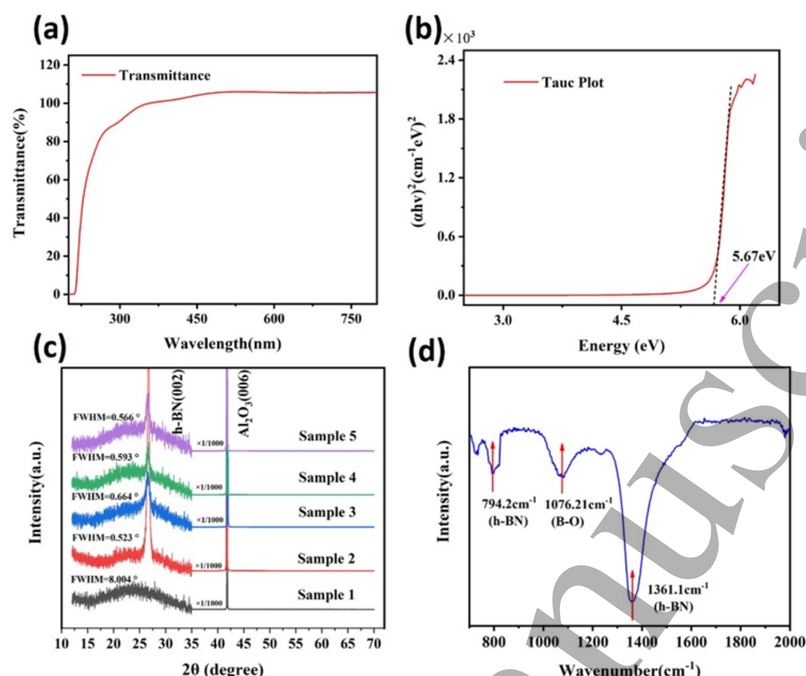
1 relatively poor film quality; and as the precursor transport process continues, the degree of
2 dehydrogenation becomes higher and higher, and the quality of the subsequent films is relatively
3 good.



4
5 Fig.4 (a) Transmission spectrum of the film sample, (b) the curve of $(\alpha hv)^2$ as a function of photon
6 energy, (c) XRD diffraction patterns of five samples in the dual temperature zone, (d) FTIR
7 spectrum of the film sample

8 The optical properties of sample 2 were characterized by UV-Vis spectrophotometer. As
9 shown in Fig 4(a), the change of the transmittance of the sample film with the incident wavelength
10 was tested, and the transmittance of the sample was close to 100% in the visible light region,
11 indicating that the surface of the film sample was relatively flat and the quality of the film crystal
12 was good. There is a steep absorption edge at 210 nm, which corresponds to h-BN. According to
13 the fitting formula of the bandgap width of the direct bandgap semiconductor, by extending the
14 tangent of the curve of $(\alpha hv)^2$ versus photon energy. The value of the intersection with the photon
15 energy axis is the corresponding optical bandgap, as shown in Fig 4 (b). The optical bandgap of
16 the sample is 5.67 eV, which is consistent with the experimental value reported by others [23].
17 Next, the crystal structure of the synthesized h-BN film was characterized by XRD. The XRD
18 results of the five sample films in the dual temperature zone are shown in Fig. 4(c). The diffraction
19 peak near 41.77 ° is from the Al_2O_3(006) plane diffraction, while the diffraction peak near 26.65 °
20 comes from h-BN (002) plane diffraction, the sample 1 at position 1 in the dual temperature zone
21 has only one broad peak, which may be due to the poor crystal quality caused by incomplete
22 dehydrogenation. As the precursor continues to transport, the dehydrogenation is more complete,
23 so the remaining 4 samples have relatively sharp diffraction peaks. The XRD peaks shown in Fig.
24 4(c) were further analyzed by FWHM, and it was found that the FWHM of sample 1 was
25 significantly higher than that of the other samples, which indicated that the quality of the other
26 four samples was relatively good except for sample 1. Since the center of the diffraction peak is
27 located at 26.65 °, the interplanar spacing calculated according to the Bragg diffraction formula
28 ($2d\sin\theta=n\lambda$) is 0.3344 nm, which is principally consistent with the 0.3328 nm interplanar spacing

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of single-crystal h-BN(002), which confirms that what we have synthesized is h-BN films. In addition, the h-BN film sample was also characterized by FTIR, and the results are shown in Fig. 4(d). The two main bands at 794.2 cm^{-1} and 1361.1 cm^{-1} are attributed to B-N stretching and B-N-B bending, which are typical features of h-BN, while the emission band near 1076.21 cm^{-1} may be caused by oxygen atoms introduced in the testing process or the growth process under low vacuum [24].

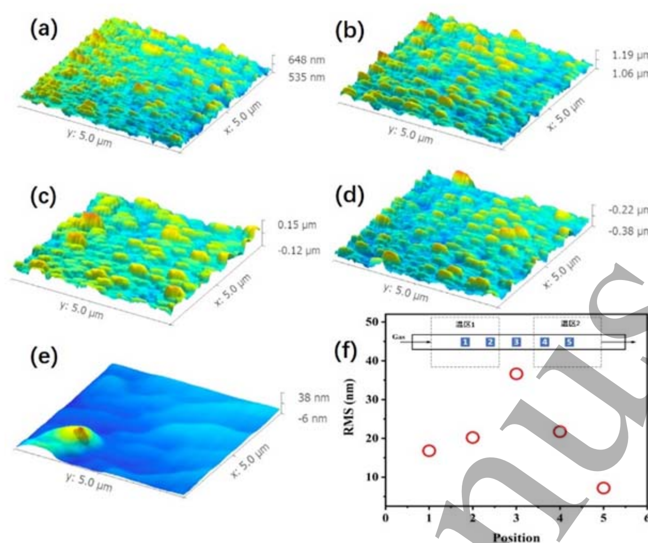

Fig. 5 (a-e) AFM results of five samples in the dual temperature zone, (f) roughness of the five samples in the dual temperature zone (the inset is a schematic diagram of the positions of the five samples in the dual temperature zone)

The surface morphology of the film samples was characterized by AFM, as shown in Fig. 5 (a-e). From the results, it can be seen that the roughness of the sample surface is closely related to the temperature. Sample 1 and sample 5 are located in the center of the two temperature zones respectively. The high growth temperature enhances the migration ability of surface adatoms, so the surface is relatively flat, while sample 3 is the farthest from the center of the two temperature zones, so it has a rougher surface. The overall roughness presents the tendency of going up firstly and going down secondly, as shown in Fig 5(f).

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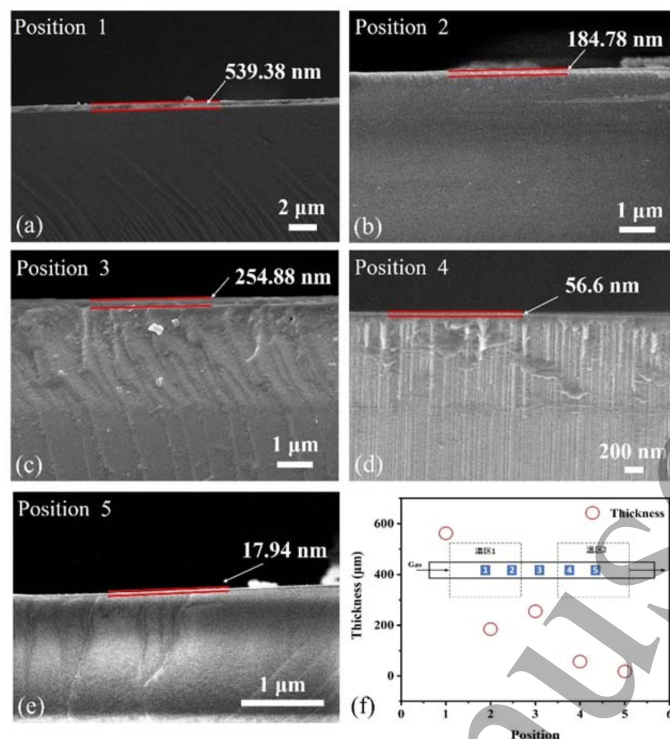

Fig.6 (a-e) SEM cross-sectional views of five samples in the dual-temperature zone, (f) the relationship between the thickness of the h-BN film and different positions in the dual-temperature zone (the inset is a schematic diagram of the positions of the five samples in the dual-temperature zone)

Finally, SEM was used to observe the thickness of the five sample films in the dual temperature zone, as shown in Fig 6 (a-e), the growth rates of the five samples at five different positions were 4.49 nm/min, 1.540 nm/min, 2.124 nm/min, 0.472 nm/min, and 0.150 nm/min, respectively. The overall thickness shows a downward trend, as shown in Fig 6 (f), the main reason may be that with the consumption of the precursor, the concentration of the precursor gradually decreases, and the nucleation rate decreases, resulting in a decrease in the growth rate. From the SEM results, h-BN thin films with a thickness of 540 nm were heteroepitaxially grown on the sapphire substrate, and h-BN was not found to be peeled off from the sapphire substrate. This situation is most likely attributed to the formation of a thin Al_xN_y layer at the interface between h-BN and Al_2O_3 when the sapphire substrate is annealed at high temperature before h-BN growth. Nitrogen atoms in N_2 replace oxygen atoms on the surface of the sapphire substrate, and then form N-Al bonds at high temperatures (greater than 1200 °C). The formation of Al_xN_y layer reduces the lattice mismatch and thermal mismatch at the interface between h-BN and Al_2O_3, and effectively relieves the stress at the interface between h-BN and Al_2O_3. Therefore, we did not find h-BN peeling from the sapphire substrate in this study.

4. Conclusion

In this paper, BN films were synthesized on sapphire substrate by the LPCVD method. Various characterization results confirmed that the synthesized films were h-BN films with hexagonal phases. The effects of the temperature field on the growth rate and quality of h-BN films were studied through samples at five different positions in the dual temperature zone. The study found that sample 1 had poor crystal quality due to incomplete dehydrogenation, and with

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the gradual consumption of precursors, the growth rates of the five samples showed a general downward trend. In addition, by studying the variation curve of $(\alpha h\nu)^2$ with photon energy, the optical bandgap of the synthesized film is 5.67 eV. This study will provide an experimental basis for growing large-area high-quality h-BN thin films.

Acknowledgement

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