Growth and characterization of uniformly distributed triangular single-crystalline hexagonal boron nitride grains on liquid copper surface

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Abstract

Single-layer hexagonal boron nitride (h-BN) is a two-dimensional (2D) material with a wide band gap and extraordinary mechanical, thermal and optical properties. It has promising applications in optoelectronics, electronics and photovoltaics. Low-pressure (150 Pa) chemical vapor deposition (LPCVD) was used to prepare uniformly distributed single-crystalline triangular h-BN grains and continuous film on liquid copper surface. A series of microscopic and spectroscopic methods were performed to characterize the morphology, crystalline structure and quality, component and thickness. It was found that h-BN grains turned into circles at higher background pressure (1000 Pa), which was due to the change in the growth mechanism from equilibrium controlled to deposition controlled. Small islands formed on primary h-BN grains because of higher concentration of precursor product. Compared to the higher background pressure, the synthetic h-BN films at low background pressure exhibited larger domain size, lower nucleation density, and no adlayer growth. Due to randomly distributed polar h-BN grains, the grain boundaries formed along the h-BN domains after merging. Typical patterns formed via the coalescence of triangular h-BN grains indicating the merging mode of growth, including edge-to-edge and edge-to-point modes. This work provides a pathway for the preparation of uniformly distributed single-crystalline h-BN grains and an in-depth understanding of the growth and merging process on liquid Cu surface.

Introduction

Single-layer hexagonal boron nitride (h-BN) is a two-dimensional (2D) material with a hexagonal lattice structure similar to graphene, consisting of alternating B and N atoms instead of C atoms [1]. h-BN has an indirect wide band gap of 5.96 eV [2] compared to graphene with a zero band gap. With alternating B and N atoms formed sp2 bonds in a plane, the h-BN has high thermal conductivity [3], high mechanical strength [4], excellent thermal stability [5]. In addition, monolayer h-BN is absent from the dangling bonds and trapped charges on surface owing to its atomically ultra-flat surface [6]. It has been reported that h-BN as dielectric layers can significantly improve the charge carrier mobility of graphene-based devices compared to direct placement of graphene on a SiO2 substrate [6–8]. In addition, h-BN can also be used in transparent and flexible electronics [9], far ultraviolet light emitting devices [10] and novel tunnelling devices [11].

The realization of scalable and controllable synthesis of h-BN films is quite important for developing practical devices. Chemical vapor deposition (CVD) is considered as the popular method for fabricating large nanosheets. Monolayer h-BN films were synthesized by ultra-high vacuum CVD system in 1995 [12]. In recent years, lots of efforts have been devoted to develop simple atmospheric pressure chemical vapor deposition (APCVD) and low-pressure chemical vapor deposition (LPCVD) methods to obtain h-BN on polycrystalline Cu foils [13], Ni foils [14], Pt foils [15], CuNi alloys [16], etc. However, h-BN preferentially forms at the defects and
grain boundaries of polycrystalline metal foils, which makes it difficult to control the thickness and quality. As an alternative, ultra-flat, defect-free liquid metal surfaces can be chosen as suitable substrates for 2D materials. The crystal nuclei will uniformly form and grow into continuous films on liquid metal surfaces. Recently, some 2D materials have been successfully synthesized on the liquid metal surfaces. The uniform monolayer, spatially self-aligned single-crystalline hexagonal graphene films were synthesized on liquid Au surface by self-collimation and electrostatic interaction [18]. A few layers h-BN films were synthesized on melted copper by APCVD [19]. Monolayer h-BN were produced by peeling off top few-layer h-BN from highly self-assembly hierarchical h-BN films synthesized on liquid Cu surface by APCVD [20]. However, the uniformly distributed triangular h-BN grains are not synthesized on the liquid metal surfaces. The coalescence mode of the as-grown grains on the liquid metal surfaces also remains unclear.

In this work, the uniformly distributed single-crystalline triangular h-BN grains and continuous films were synthesized on liquid Cu surface by using LPCVD method at a low pressure of 150 Pa. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, UV–visible spectroscopy (UV–vis) and transmission electron microscopy (TEM) were used to characterize the morphology, crystalline structure and quality, component, thickness, etc. The h-BN was also synthesized at higher pressure (1000 Pa) in order to compare the difference. Smaller circular h-BN grains with adlayer islands formed on liquid Cu surface at higher background pressure with increasing the Ar and H₂ mixed gases flow. Therefore, low background pressure is conducive to grow uniform and larger grain monolayer h-BN on liquid Cu surface. Clear grain boundaries were observed along the h-BN domains on continuous films, which provided insight into the growth and merging process of h-BN. Typical patterns composed of triangular h-BN grains can be explained by edge-to-edge and point-to-edge modes. This provides a deep fundamental understanding of h-BN growth process. This work gives a pathway for the preparation of high-quality h-BN films on liquid Cu surface.

Experiment section

Growth

Copper foils (Alfa Aesar, 0.025 mm thick, annealed, uncoated, 99.8% purity) and molybdenum foils (Alfa Aesar, 0.1 mm thick, 99.95% purity) were cleaned by ultrasonic for 10 min in hydrochloric acid, ethanal and deionized water, respectively. Then they were oven dried and cut into 15 mm × 15 mm pieces. Two pieces of Cu foils were placed on one piece of Mo foil in corundum boat, and the whole stack was placed into quartz glass tube with a diameter of 80 mm. About 50 mg ammonia borazine (Sigma Aldrich, 97% purity) was placed in iron boat as precursor. Before heating up, the LPCVD system was pumped up to 10 Pa, and then filled with Ar gas (99.999%) to atmospheric pressure. This process was repeated three times. The tube furnace was heated to 1100 °C, and the iron boat containing ammonia borazine was pulled to the area where heating belt was wound on the quartz glass tube (the temperature of heating belt was 90 °C). When the growth process ended, the corundum boat was moved from high temperature zone to room temperature zone.

A 2:1 mixture of Ar:H₂ (99.999%) with flow rates of either 80:40 standard cubic centimeters per minute (sccm) or 300:150 sccm is used as a carrier gas to transport the precursor onto the liquid Cu surface. Two different background pressure conditions were investigated: (1) Low pressure: 80 sccm Ar and 40 sccm H₂, the background pressure is 150 Pa; (2) Higher pressure: 300 sccm Ar and 150 sccm H₂, the background pressure is 1000 Pa.

Transfer

The as-grown h-BN was transferred to target substrate using poly (methyl methacrylate) (PMMA)-assisted electro-chemical bubbling method. PMMA (6 wt% in anisole solution) was spin-coated at 1000 rpm for 1 min on the h-BN/Cu/Mo and then dried for 2 h. The PMMA/h-BN/Cu/Mo was connected to the cathode of power supply, and Pt foil was connected to the anode of power supply. Then they were placed in NaOH solution (1 mol l⁻¹) for electrolysis with a current of 1 A. As the electrolysis started, H₂ continuously generated at the cathode emerging from the surface of metal substrate, causing PMMA/h-BN to fall off from the metal substrate. Finally, the h-BN/PMMA was purified by deionized water and scoop onto target substrate. The h-BN/PMMA on target substrate was tilted to dry in air. The samples were immersed in acetone for 1 h to remove PMMA.

Characterization

The h-BN grains/films were characterized by scanning electron microscopy (HITACHI SU8220, operated at 5 KV), optical microscope (Shanghai Huitong XPL 1500), Raman spectroscopy (Renishaw in Via, 532 nm laser), X-ray photoelectron spectroscopy (PANalytical AXIOS, Al Kα radiation), transmission electron microscopy (JEOL JEM-2100F, operated at 200 KV) and UV–visible spectrophotometer (PERKINELMER Lambda 950).
Results and discussion

The h-BN was grown on liquid copper surface by LPCVD system as schematically illustrated in figure 1. Solid ammonia borane (BH$_3$-NH$_3$) was used as precursor. In the experiment, the BH$_3$-NH$_3$ was heated to sublimate by a heating belt wrapped around the quartz glass tube. The BH$_3$-NH$_3$ powders were placed in an iron boat which can be moved by a magnet to the desired location. When the heating belt was heated to the certain temperature (90°C), it was convenient to move the iron boat by a magnet to the position where the heating belt was wound up, so as to accurately control the heating time and avoid the sublimation of the precursor during the heating process.

Prior to the growth of h-BN, Cu foils and Mo foils were cleaned by ultrasonic in hydrochloric acid, ethanal and deionized water to remove the native oxide and attached contaminations. Two pieces of the treated Cu foils were placed on the top of one piece of the treated Mo foil, and then the entire stack was placed in corundum boat. The corundum boat was connected to the iron block by the Fe-Cr-Al wire in order to be moved by pulling the iron block by a magnet. At the end of growth process, the corundum boat was moved from the high temperature heating zone to the room-temperature zone by pulling the iron block to quickly terminate the growth reaction and realize rapid cooling.

Before starting the tubular furnace for heating, argon gas was used to clean the quartz glass tube three times to remove the residual air. The gas mixture of 80 sccm Ar and 40 sccm H$_2$ was introduced to tubular furnace, and the background pressure was maintained at 150 Pa by a vacuum pump. A higher background pressure (1000 Pa) was obtained by increasing the Ar and H$_2$ mixed gases flow (300 sccm Ar and 150 sccm H$_2$).

Before feeding the BH$_3$-NH$_3$, the temperature of heating zone of tubular furnace was kept at 1100°C for 20 min to ensure that the Cu foil was completely melted and evenly distributed on the Mo foils. The good wettability between liquid Cu and Mo ensures a flat and uniform surface and provides a suitable platform for h-BN growth [21]. And then, the iron boat containing ammonia borazine was pulled with a magnet to the area wrapped by heating belt when the temperature reached 90°C. With the sublimation of precursor, h-BN started to grow on the liquid Cu surface. The corundum boat was pulled out of the growth zone to achieve rapid reaction termination and cooling.

Figure 2 shows the scanning electron microscopy (SEM) images of the h-BN on liquid Cu surface with different growth time at low pressure of 150 Pa. Previous works have revealed that h-BN grains preferentially nucleate at crystallographic defects of catalyst substrate surface of solid Cu, which consequently leads to few-layer h-BN films [19, 21]. Our work shows that the h-BN grains can nucleate uniformly on ultra-flat and defect-free liquid Cu surface. In contrast to the growth on typical polycrystalline Cu foils, where the h-BN grains are disorderly distributed [13, 22], here the h-BN grains form uniformly with perfectly triangular grains on liquid Cu surface. We also found no adlayer growth under low pressure compared to h-BN films grow on liquid Cu surface under ambient pressure [20, 23]. As shown in figure 2(a), the shapes of uniformly distributed h-BN grains are nearly perfect equilateral triangles, indicating that these grains are single crystals with nitrogen-terminated zigzag edges [24].

With increase in the growth time, the single-crystalline h-BN grains gradually covered the whole liquid Cu surface, and finally merged into continuous films (figure 2(b)). Due to the random nucleation and orientation of polar h-BN grains on the liquid Cu surface, when they became a large continuous film, grain boundaries [25] formed as shown in figures 2(b), (c). Figure 2(d) shows the optical image of h-BN films grown on liquid Cu surface. The triangular h-BN grains and grain boundaries can be clearly observed.

With further increase in the growth time, secondary nucleation took place on the grown monolayer h-BN films. From figure 2(e), it can be seen that secondary nucleation is concentrated on the central area of triangular
h-BN grains. Similarly, the h-BN islands formed by secondary nucleation have clear triangular shape. In figure 2(f), the large-scale patterns formed by triangular h-BN islands uniformly distribute on the whole h-BN films after continuing to extend the growth time.

**Figure 2.** (a) SEM image of the uniformly distributed triangular h-BN grains grown on liquid Cu surface (3 min growth time). (b) SEM image of continuous h-BN films composed of stitched triangular h-BN grains on liquid Cu surface (5 min growth time). (c) High magnification SEM image of continuous h-BN films. Due to randomly distributed polar h-BN grains, grain boundaries (white boundaries) were formed along the h-BN domains after merging. (d) Optical image of continuous h-BN films with evident grain boundaries. (e), (f) Adlayer islands were formed on the h-BN films (7 min and 10 min growth time) with increase in growth time. The inset in figure (e) shows that the shape of the h-BN islands formed by secondary nucleation is triangular. (g) Schematic diagram of the growth process of h-BN on the surface of liquid Cu substrate.
The growth process of h-BN films on the liquid Cu surface at low pressure can be explained by Stranski-Krastanov model [26], as shown in figure 2(g). Initially, uniformly distributed triangular single-crystalline h-BN grains form on the ultra-flat and defect-free liquid Cu surface at low pressure. With increasing growth time, triangular single-crystalline h-BN grains gradually grow up and merge into continuous films with grain boundaries. With further increasing growth time, secondary nucleation occurs in the central triangular h-BN grains, forming triangular h-BN islands that gradually assemble to large-scale patterns.

The quality, component, thickness, and structure of h-BN films were further characterized. In order to confirm the elemental composition of as-grown h-BN films on the liquid surface, we performed x-ray photoelectron spectroscopy (XPS) characterization as shown in figures 3(a), (b). The peaks are observed at 190.6 eV and 398.2 eV, which correspond to typical B 1 s and N 1 s peaks [27], respectively. The atomic ratio of B/N calculated from the integrated peak areas and the peak sensitivity factors is about 1:1.1, which is very close to the theoretical ratio of 1:1. At the same time, the binding energy spectra of N 1 s and B 1 s also show the existence of B-N sp2 bond, indicating hexagonal phase in the grown BN films [13].

The h-BN was transferred to SiO2/Si substrate using PMMA-assisted electro-chemical bubbling method [15] to perform Raman spectroscopy characterization. Figure 3(c) shows the peak of Raman shift of the h-BN films on SiO2/Si substrate at 1372 cm\(^{-1}\), which agrees well with the boron-nitrogen bond E\(_{2g}\) stretching. The blue shift in the Raman spectrum may be due to compressive strain and wrinkle formation, which cause strain in film and harden the E\(_{2g}\) phonons [4, 19]. Since the thermal expansion coefficient of h-BN is negative, it will form wrinkles after cooling [28, 29]. The weak intensity is consistent with the monolayer h-BN [19, 30, 31].

The good optical property of h-BN films in the deep ultraviolet region makes it a promising candidate in optoelectronic and electronic fields. The same method was used to transfer h-BN films to quartz glass for performing absorption spectrum of h-BN films by UV-Visible spectroscopy (UV-vis). The absorbance of the h-BN films in the visible light region is very low, as shown in figure 3(d). There is only one abrupt absorption peak at 202 nm. The deduced optical bandgap (OBG) was calculated to be 5.90 eV, which corresponds to the value of monolayer h-BN predicted by theoretical calculations [2].

Transmission electron microscopy (TEM) combined with selected area electron diffraction (SAED) was used to characterize the crystallinity and structure of h-BN films. The PMMA-assisted electro-chemical bubbling method was also used to transfer h-BN films to holey carbon TEM grids. Figure 4(a) shows the low magnification TEM image of a typical triangular h-BN grain. Three different locations of a single h-BN grain (marked by red dotted circle) were selected to perform SAED. As shown in figure 4(b), only one set of
characteristic six-fold symmetric diffraction pattern is found, indicating the h-BN grain is single crystal and hexagonal structure [32]. Figure 4(c) illustrates the TEM image of h-BN films covering the hole in TEM grid. The single-layer thickness of h-BN film was measured by high resolution TEM (HRTEM) at the edge of h-BN [28, 33], as shown in figure 4(d).

At the heating belt temperature of 90 °C, solid ammonia borane decomposes into hydrogen, polyiminoborane (BHNH; solid), and borazine ((HBNH)3; gas) [34, 35]. At the background pressure of 150 Pa, the borazine was carried by Ar and H2 flow to deposit on the liquid Cu surface in the quartz glass furnace, and then dehydrogenate to produce h-BN at 1100 °C. At low background pressure, the bonding force between borazine molecules and grown h-BN grains is weak. Any precursor molecules adsorbed on the grown h-BN grains will be quickly desorbed back into the gas phase [15, 36]. Thus, uniform, single-crystalline h-BN grains can be synthesized on liquid Cu surface.

In order to study the effect of pressure on the growth of h-BN, figure 5 shows the SEM image of h-BN with different growth time at a background pressure of 1000 Pa with increasing the Ar and H2 mixed gases flow (300 sccm Ar and 150 sccm H2). It can be observed that the shape of h-BN grains changes from triangle into circle and h-BN islands were aggregated on the circular h-BN grains. With increase in Ar and H2 mixed gases flow, more
precursor products were carried to deposit on liquid Cu surface at higher background pressure. The growth of h-BN grain was promoted by high concentration of precursor products, and the deposition/decomposition rate of inflow was faster than the consumption of each reaction site at the growth front, resulting in isotropic circular patterns [21]. Therefore, the growth of h-BN has changed from equilibrium controlled to deposition controlled [21] at higher precursor products flux, which results in different h-BN shapes. Similarly, with more precursor products adsorbed on the grown h-BN grains surface, they are difficult to desorb into the gas phase, so the influx reactants can react at higher energy barriers [21], resulting in forming h-BN islands. With increasing growth time, the h-BN grains gradually merged into continuous films with small h-BN islands, as shown in figure 5(b). The adlayers are distributed in island-like manner on the first layer, which is mainly due to the difficulty of

Figure 5. (a) SEM image of uniform circular h-BN grains with small islands on liquid Cu surface at higher background pressure (1000 Pa, 3 min growth time). (b) SEM image of continuous h-BN films with small islands on liquid Cu surface at higher background pressure (1000 Pa, 5 min growth time).

Figure 6. (a) Continuous h-BN films composed of stitched triangular h-BN domains at low background pressure (150 Pa). (b) Statistical distributions of triangular h-BN grain sizes from figure (a). (c) Continuous h-BN films composed of stitched polygonal h-BN domains at higher background pressure (1000 Pa). (d) Statistical distributions of polygonal h-BN grain sizes from figure (c).
surface diffusion of the adlayer h-BN clusters on the first h-BN layer [37], making it difficult to form uniform multilayer h-BN film.

The triangular and polygonal h-BN domains at different pressure can be clearly observed from figures 6(a), (c), respectively. The statistical distributions of the triangular and polygonal h-BN grain sizes from figures 6(a), (c) are shown in figures 6(b), (d). The mean grain size is ~150 μm² for h-BN grown at low background pressure, which is about 7 times larger than that of ~20 μm² at higher background pressure. Obviously, compared to higher background pressure, the lower nucleation density, larger crystal grain and no adlayer growth were obtained at low background pressure.

Figure 7(b) shows the statistical distributions of relative orientation angle θ for triangular h-BN grains in figure 7(a). θ is the minimum angle required to rotate any triangle clockwise to a position where one side is parallel to the horizontal axis and one angle is above the parallel side. Since the h-BN grains are nearly equilateral triangles, the range of θ is 0–120°. The orientations of triangular h-BN grains are not preferred and the numbers of triangular h-BN grains in each orientation are almost equal. This is quite different with the h-BN grains grown on solid Cu surface. It has been reported that the h-BN grains grown on solid Cu faces show preferred lattice orientations with minimum stacking energy due to the different stacking energy at different orientation angles [38, 39]. However, when the solid Cu foil melts into liquid, the Cu crystal faces disappear, which results in random orientations of h-BN grains.

Intriguingly, various complex patterns were generated when the uniform triangular single crystal h-BN grains grew into continuous films. The grain boundary lines can be clearly seen, which is the result of merging between randomly distributed polar h-BN grains. When two h-BN grains with same nitrogen-terminated zigzag edges are merged, seamless stitching cannot occur [40]. From grain boundaries in figure 7(c), we can gain insight into the different coalescence processes of h-BN grains.
Figure 7(d) shows a series of typical patterns composed of h-BN grains extracted from figure 7(c). When the random triangular h-BN grains grow up and merge, there are generally two merging modes, namely, edge-to-edge and point-to-edge [41]. Figure 7(e) shows four merging modes according to SEM images combined with previous literature reports [40, 41]. When the adjacent h-BN grains are certain far away, they gradually grow up and follow the edge-to-edge merging mode. However, when adjacent triangular h-BN grains are closer to each other, they follow the point-to-edge merging mode, which is consistent with the distances between the complete triangle h-BN grains and between the triangular and the smaller intrusive h-BN grains in the figure 7(c). In addition, almost secondary nucleation occurs in the point-to-edge mode, and the nucleation site is located on the intruded point due to faster adatom diffusion at the tip of intrusion than the flat edge [42].

Conclusions

In summary, monolayer h-BN films were successfully synthesized on liquid Cu surface by LPCVD. The h-BN grains were uniformly distributed and randomly oriented as there were no defects, grain boundaries and crystal face on the liquid Cu surface. The growth process of h-BN films on liquid Cu surface can be explained by the Stranski-Krastanov model at low pressure. At higher background pressure, circular h-BN grains with adlayer islands were observed owing to the change in growth mechanism, from equilibrium controlled to deposition controlled at higher precursor product concentration. Lower nucleation density, larger h-BN grains and no islands were observed owing to the change in growth and merging process of h-BN grown on liquid Cu surface. This work provides an in-depth understanding of growth and merging mechanism of h-BN, and paves the way for the growth of high-quality h-BN films.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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