Few-layer hexagonal boron nitride synthesized by chemical vapor deposition and its insulating properties

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Abstract

Hexagonal boron nitride (h-BN), which is one of two-dimensional (2D) materials, is expected to be used as supporting and passivation layers for graphene-based devices. However, it is difficult to obtain large-area h-BN by the conventional exfoliation techniques. Here, we performed chemical vapor deposition (CVD) by employing epitaxial metal films as a catalyst to grow few-layer h-BN with a large grain size. The grain sizes of h-BN obtained were found to be a few micrometers or larger. Furthermore, we evaluated insulating properties of few-layer h-BN with conductive atomic force microscopy. Assuming a parallel plate model, a breakdown strength was estimated to be at least 7.5–45.5 MV cm$^{-1}$, considering variations in h-BN thickness. These values are comparable with that obtained for exfoliated h-BN in a previous study. Considering the scalability and insulating properties, our epitaxially-synthesized h-BN is expected to be used for future graphene devices.

Introduction

Two-dimensional (2D) materials including graphene and transition metal dichalcogenides are attracting a lot of attention as future electronic materials due to their unique structure and physical properties. Graphene has extremely high electron and hole mobility, suggesting that it can be used as a channel material for field effect transistors (FETs) in the near future [1]. Hexagonal boron nitride (h-BN), which is also one of 2D and layered materials, is well known as a prominent candidate for a supporting and/or passivation layer of graphene-based devices, because graphene supported by h-BN can maintain its excellent electrical properties [2].

In order to apply h-BN to insulating/passivating layers for graphene-based devices, it is necessary to obtain uniform and flat h-BN films all over a large wafer. In this respect, exfoliation from a h-BN crystal is not a good method because of difficulties in controlling the size and position of h-BN flakes. Chemical vapor deposition (CVD) is one of suitable technologies because it is scalable. Synthesis of single-layer h-BN by thermal decomposition of borazine gas in an ultra-high vacuum chamber has been performed on metal crystal surfaces [3–8] since 1995. In these cases, h-BN was limited to the size of metal crystals, which is typically smaller than a few centimeters. Recently, synthesis of single-layer and/or few-layer h-BN has been reported using metal foils and metal films [9–25], which is more scalable than using metal crystals. Actually, synthesis of a single crystal h-BN island with a domain size of 7500 μm$^2$ on Cu-Ni foil was reported [18]. However, this domain size is not large and continuous enough to be used for graphene-based devices fabricated all over a large wafer, because it is difficult to control the positions of domain boundaries that may degrade the reliability of devices.

Recently, epitaxial synthesis of single-layer h-BN with an epitaxial metal catalyst film on sapphire substrate was reported [14, 23], aiming at uniform h-BN synthesis with no grain boundaries. In the case of graphene, it has been found that single-layer and multi-layer graphene can be grown epitaxially on an epitaxial cobalt film due to good lattice matching between cobalt and graphene [26, 27], in which the low electrical resistivity of multilayer-graphene synthesized with the epitaxial cobalt film comparable to that of HOPG [27]. This may be a key technique to achieving uniform few-layer h-BN synthesis.
To utilize h-BN as an insulating layer for transistors or other electronic devices, breakdown strength is an important parameter to address. Recently, layer-by-layer breakdown of h-BN thin films exfoliated from h-BN samples synthesized by a temperature gradient method under high pressure and high temperature was reported. The breakdown electric-field strength of exfoliated h-BN was estimated to be ∼12 MV cm⁻¹. The insulating properties of h-BN synthesized by CVD were also reported to be several MV cm⁻¹ which was much lower than that of exfoliated h-BN. As the cause of the difference, the polycrystalline structures of the h-BN films giving a leakage path through grain boundaries were suggested. Therefore, the h-BN synthesized epitaxially is expected to show much better the insulating properties.

In this study, we employed an epitaxial Cu film to synthesize few-layer h-BN by thermal CVD method and evaluated it by several methods. Since it is often said that the quality of CVD-grown two-dimensional film is poorer than that of exfoliated film, we put special emphasis on evaluating its quality. We actually evaluated insulating properties of CVD-grown few-layer h-BN film, which is very important for application of h-BN film to devices using two-dimensional materials such as graphene.

**Experimental**

Hexagonal boron nitride was synthesized by the thermal CVD method on epitaxial copper (Cu) films, which were formed by sputtering on 3-inch sapphire substrate (c-surface). The thickness of Cu films used was 1000 nm. The thermal CVD process was performed in a low pressure chamber (Aixtron K.K. Black Magic CRIUS-R), in which NH₃ and B₂H₆ diluted by H₂ and Ar were used as the source gas. The total pressure and substrate temperature during the CVD process were approximately 500 mbar and 1100 °C, respectively. The mass flow rate of NH₃, B₂H₆, H₂ and Ar were 1, 0.2, 500 and 4500 standard cubic centimeters per minute (sccm), respectively. Furthermore, to analyze the sample in detail, the synthesized h-BN was transferred to a TEM grid and a silicon (Si) substrate with a 90-nm-thick thermal silicon dioxide (SiO₂) layer. The transfer process was similar to that used for graphene.

The synthesized h-BN was analyzed by Raman spectroscopy (Horiba Jovan-Yvon; Laser excitation wavelength: 488 nm), electron backscattered diffraction (EBSD; JEOL JSM-6500F), transmission electron microscopy (TEM; Hitachi H-9000UHR III or FEI Tecnai Orisis), scanning electron microscopy (SEM; Hitachi S-4800) and X-ray photoelectron spectroscopy (XPS, PHI QuanteraSXM, Incident X-ray energy: 1486.6 eV (Al), Emission angles: 15° relative to the surface normal direction). The insulating properties were evaluated by conductive atomic force microscopy (C-AFM; Shimazu SPM-9700).

**Results and discussions**

Figure 1 (b) shows the inverse pole figure (IPF) map of a Cu film on a c-plane sapphire substrate observed after CVD synthesis by EBSD. The IPF image suggests no grain boundaries on the catalyst film within experimental resolutions. Furthermore, the IPF map normal to the surface reveals that Cu film is highly oriented in the (111) direction normal to the surface, implying that highly oriented fcc (111) Cu film was used as a catalyst.

After synthesis, it was found that the sample had no contrast in the optical microscope images (not shown). There seemed to be no signal either in the Raman spectrum of the as-grown sample, except for background signal as shown in figure 2 (a). The Raman spectrum in figure 2 (b) measured after being transferred onto a
h-BN synthesized by epitaxial copper feedstock, that is NH₃ and B₂H₆ or ammonia borane reported previously approximately corresponding to the stoichiometric composition ratio of h-BN and matching with the value formation on Cu catalyst before in the case of bulk h-BN without additional peaks were observed at binding energies of 190.4 eV and 398.0 eV, which had been reported as-grown sample might be caused by stronger background intensity originated from Cu h-BN, because thinner h-BN is reported to have a very weak Raman signal can see single-layer and bi-layer h-BN clearly as shown in sectional image of h-BN was observed by TEM analyses. Figure 2(h-BN synthesis, because the solubility of B and N in copper is known to be different allotropes\[11\]. The result of XPS of as-grown h-BN. (c) and (d) The results of XPS of as-grown h-BN. (e) A cross sectional TEM image of as-grown h-BN. (f) SEM image of as-grown h-BN.)

Figure 2. (a) and (b) Raman spectra before and after being transferred onto a SiO₂/Si substrate. After transfer, E₂g peak (●) originated from h-BN and two peaks (▲) from the substrate are observed. The inset is also an enlarged E₂g peak with a fitting curve. The FWHM of the E₂g mode is well known to be originated from crystallinity of h-BN, although this value seems to be different from that of single-layer h-BN [11]. The E₂g peak was also fit with Lorentzian shown in the inset. The single Lorentzian and its peak position supports h-BN synthesis without BN allotropes [11]. The FWHM described above is larger than those of exfoliated h-BN [31], it is smaller than those of h-BN synthesized with CVD methods [10, 11, 15, 21, 24]. This implies to h-BN synthesis with high quality.

Figures 2(c) and (d) shows XPS spectra of as-grown h-BN. The single B 1 s and N 1 s core level spectra without additional peaks were observed at binding energies of 190.4 eV and 398.0 eV, which had been reported before in the case of bulk h-BN [32] and h-BN on Cu [6, 9, 10, 15, 16, 21, 22]. These observations indicate h-BN formation on Cu catalyst films. The atomic ratio (B/N) of B and N was estimated to be 1.1 from the XPS spectra, approximately corresponding to the stoichiometric composition ratio of h-BN and matching with the value reported previously [9, 10, 15, 16, 21, 22]. Although this value seems to be different from that of single-layer h-BN synthesized by epitaxial copper films [23], it may be originated from different methods to supply feedstock, that is NH₃ and B₂H₆ or ammonia borane [23]. The more amount of N than B is probably better to h-BN synthesis, because the solubility of B and N in copper is known to be different [16]. Furthermore, a cross-sectional image of h-BN was observed by TEM analyses. Figure 2(e) indicates that bi-layer and/or tri-layer h-BN was actually formed on Cu film. The more amount of N than B is probably better to h-BN synthesis, because the solubility of B and N in copper is known to be different [16]. Furthermore, a cross-sectional image of h-BN was observed by TEM analyses. Figure 2(e) indicates that bi-layer and/or tri-layer h-BN was actually formed on Cu film. The SEM image in figure 2(f) after synthesis suggests some synthetic materials, that is h-BN, with different contrasts, indicating different layers such as TEM images. Most of the lines in the SEM image are originated from wrinkles in h-BN film, which was also observed in h-BN on Cu [23].

Figure 3 shows TEM images of h-BN observed after being transferred to a TEM grid from the substrate. One can see single-layer and bi-layer h-BN clearly as shown in figures 3(a) and (b). The interlayer distance of bilayer h-BN was estimated to be ~0.33 nm, matching that reported previously [11, 12]. Taking into account several cross-sectional TEM images, it was found that the about 92% of h-BN film had one to three layers, as shown in figure 3(c). Diffraction patterns in figure 3(c) derived from a bright field (BF) image (figure 3(d)) suggest that the sample is of a single crystal at least in the view of the BF image. In addition, this uniform BF image suggests almost uniform synthesis of h-BN films without any contaminations caused by the transfer process. At the same position, a dark field (DF) image was also observed as shown in figure 3(f). The contrast of the DF image of h-BN
looks almost the same, suggesting that the orientation of h-BN was almost the same within this DF image. In other words, few-layer h-BN with a micrometer-sized single grain was obtained. These results suggest that epitaxial synthesis of few-layer h-BN without grain boundaries has been realized, which can be beneficial to graphene-based devices.

The insulating properties of few-layer h-BN were evaluated by C-AFM. The sample voltages varied from 0 to −10 V, in order to prevent anodization of the sample. Observed area by AFM was 100 nm², as shown in figure 4(a). Current images measured at the sample voltages of 0, −1.0, −2.0 and −3.0 V were also shown in figures 4(b)–(e). Although the current images seemed to be the same for 0 to −2.0 V, one can see white colored regions observed at −3.0 V, suggesting a breakdown of h-BN. Current-voltage characteristics shown in figure 4(f) also shows a breakdown at the voltage of −3.5 V. By measuring IV characteristics at several different positions, breakdown voltages were found to vary from −3.0 to −4.0 V. Although it is difficult to estimate the layer number of h-BN from the AFM images, the stable breakdown voltages imply the uniformity of h-BN film, supporting the results obtained by TEM observations. Assuming our setup used for C-AFM measurements as a parallel plate model, the breakdown electric field corresponding to a breakdown voltage of −3.0 V and thicknesses from one to six layers was estimated to be in the range of 7.5–45.5 MV cm⁻¹, considering variations in h-BN thickness shown in figure 3(c). In our assumption, the distance between h-BN and two electrodes, that is a catalyst film and an AFM tip, is regarded as an interlayer distance of h-BN for simplicity. The estimated value of the breakdown electric field is equivalent or higher than that for exfoliated h-BN reported previously [28, 33]. Furthermore, it is also found to be much higher than those for h-BN obtained with the CVD methods [13, 19, 20, 22]. These results suggest that few-layer h-BN synthesized epitaxially by thermal CVD is comparable in quality to that obtained by the temperature gradient method [34]. Although the breakdown measurements were done with C-AFM in this study, bulk-scale breakdown measurements would be preferable. We are planning to perform such measurements in future studies.

It is not clear yet why our CVD h-BN with epitaxial films has a higher breakdown strength. However, we consider that the differences of h-BN synthesized epitaxially from those with copper foils might be originated from different crystalline quality of h-BN taking account of Raman spectra. In addition, it was reported that the grain density of h-BN originated from epitaxial films [23] seemed to be smaller those from copper foils [16] at
the first stage of CVD process, which implies to a small number of the grain boundaries of h-BN from epitaxial films. Furthermore, layer-by-layer breakdown of h-BN thin films, which was observed previously [33], was not observed in our case. This may be due to differences in the numbers of irreversible defects [33], which should depend on the growth processes. Further studies would be necessary to elucidate what determines the breakdown strength of h-BN.

Conclusion

Hexagonal boron nitride (h-BN) is a good candidate for a supporting/passivation layer of graphene-based devices. Here, we succeeded in growing few-layer h-BN films with micrometer-sized grains by employing epitaxial catalyst Cu film in thermal CVD. About 92% of h-BN film was estimated to have one to three layers from TEM observations. Furthermore, we elucidated insulating properties of h-BN by C-AFM. Assuming a parallel plate model, the breakdown electric field was estimated to be 7.5–45.5 MV cm$^{-1}$ at least. Epitaxially-synthesized h-BN is expected to help graphene find real-world device applications in the near future.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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