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## 主 論 文 の 要 旨

### 論文題目

**Synthesis of hexagonal boron nitride by  
metalorganic chemical vapor deposition for  
advanced semiconductor devices**

(次世代半導体デバイス創成のための有機金属化合物気相  
成長法による六方晶窒化ホウ素の合成)

氏 名 楊 旭

### 論 文 内 容 の 要 旨

Hexagonal boron nitride (h-BN), a two-dimensional layer-structured group-III nitride, has shown enormous potential for high-performance device fabrication as well as the technology innovation. Because of high flexibility and compatibility, metalorganic chemical vapor deposition (MOCVD) is regarded as one of the most promising approaches to synthesis of h-BN for future versatile applications. However, the epitaxial growth of device-ready h-BN films on microfabrication-compatible substrates (e.g. Sapphire, SiC, III-nitrides) is very challenging. Working is ongoing but still in preliminary stage. Investigation and understanding of the nucleation and growth behaviors of h-BN on those commonly used dielectric substrates have been quite important. In this thesis, thereby, epitaxial growth of h-BN on sapphire and III-nitrides by MOCVD is systematically explored.

First, h-BN grown on sapphire substrate is systematically investigated in Chapter 3. Two kinds of

growth techniques, i. e. conventional continuous-mode MOCVD and pulsed-mode MOCVD are employed and investigated to synthesis of h-BN on sapphire substrates. Based on the investigation in conventional continuous-mode MOCVD growth, it can be firstly seen that large V/III ratio facilitates to form 2D h-BN layer at high temperature with flat surface and extremely low growth rate (~2 nm per hour). On the contrary, the reduced V/III ratio is able to significantly enhance the growth rate, but causing the remarkable degradation in surface morphology and crystalline quality. Either low growth efficacy or poor crystallinity in BN film is the big issue in continuous-mode MOCVD of h-BN. In order to overcome the problems, the improved growth process is required for h-BN epitaxy. Compared with continuous-mode MOCVD, improved crystallinity and enhanced growth efficacy are demonstrated in pulsed-mode MOCVD growth technique. In this case, the impact of fundamental growth parameters such as growth temperature, V/III ratio and the pulsed duration on BN material properties is studied in detail. Consistent with the results achieved in continuous-mode growth, it is suggested that h-BN growth favors high temperature and large V/III ratio. The best condition is when just enough  $\text{NH}_3$  is supplied to fully convert the TEB within per pulsed cycle. Excess  $\text{NH}_3$  caused islands on h-BN film surface while a lack of  $\text{NH}_3$  almost does not form h-BN at all. Despite the low growth rate per cycle, additionally, we investigated the effect of injection sequence of precursors on BN films growth. After growth of 600 cycles, nonetheless, there is no visible difference either in surface morphology or XRD scan for both h-BN layers. Whichever precursor (TEB or  $\text{NH}_3$ ) is supplied first in the growth cycle, it should be noted that the unintentional nitridation of sapphire substrate is inevitable especially during the initial stage of growth. This may weaken the impact caused by simply switching TEB and  $\text{NH}_3$  injection sequence at short supply duration. In particular, the very slow growth rate of BN with short injection duration of TEB and  $\text{NH}_3$  makes nitridation even less different for both cases above. But it could be expected that the change would most likely be presented if an intentional surface pre-treatment by TEB or  $\text{NH}_3$  with a longer injection time (tens of seconds or longer) before starting growth. Actually, the growth of h-BN on sapphire are affected by pre-nitridation of sapphire has been reported in previous studies. Based on the experimental results, at optimum conditions, the wafer-scale and single-crystal h-BN layers with uniform thickness are successfully achieved using pulsed-mode MOCVD growth.

The epitaxial alignment between the h-BN film and sapphire substrate is examined by electron backscatter diffraction for ~60-nm-thick h-BN sample grown at temperature of 1330°C. The pole

figures show intense (0001) reflections at the center, indicating highly *c*-oriented h-BN is formed. In addition, clear sixfold-symmetric features in (11-20) and (10-10) views are observable, which demonstrates that hexagonal phase BN is formed in this work. It is also confirmed that the alignment between the h-BN layer and the sapphire substrate is  $[0001]_{\text{h-BN}} \parallel [0001]_{\text{sapphire}}$  and  $[10-10]_{\text{h-BN}} \parallel [11-20]_{\text{sapphire}}$ , which is in agreement with previous reports that 30° rotation between epitaxial h-BN and sapphire for in-plane alignment. Moreover, h-BN as a promising candidate for deep UV optoelectronic applications, the optical properties is investigated as well for the h-BN films grown on sapphire. The significant absorption at around ~210 nm is visible. The significant absorption is associated to the band edge transition. The absorption coefficients (expressed in  $\text{cm}^{-1}$ ) of about 60 nm thick BN films are calculated to be going to  $10^6$  levels above the bandgap energy, indicating BN films has high oscillator strength for the bandgap transition. Furthermore, the largest optical direct bandgap among in h-BN film in this study is extracted to be ~5.80 eV. It should be noted that because the growth of high-quality h-BN crystals is still challenging, consensus has not been established even for the fundamental material properties in h-BN. Both direct and indirect bandgap properties for h-BN have been reported in previous studies based on experiments and theoretical calculations. It remains an open question so far. The possible explanation for the controversy could be given, including that the strain state can tune the nature of electronic structure, and hence causing the change between indirect bandgap and direct bandgap. Moreover, the stacking sequence of h-BN may also induce different bandgap types. Overall, more investigation is required to figure out the optical properties of h-BN, but the h-BN layers achieved in this work with direct band transition behavior and large band edge absorption at ~5.80 eV will be useful for the development of UV or deep UV light emitters

The growth evolution of h-BN epilayer on sapphire in terms of surface and interface properties is further investigated in Chapter 4. Particularly, an unexpected interfacial amorphization at h-BN/sapphire interface is found. To understand the driving force for the formation of the amorphous interlayer, EELS is performed to probe the chemical composition and bonding structure in the epitaxial film. EELS in both layers show  $\pi^*$  and  $\sigma^*$  energy-losses in B *K* and N *K* edges that are characteristic  $sp^2$ -bonded BN, which is consistent with an h-BN. Furthermore, there are no obvious differences in the fine structures among the B *K* and N *K* peaks for the amorphous BN interlayer and topside h-BN layer, but the intensity ratio between  $\pi^*$  and  $\sigma^*$  differs between them.

Hence significantly reduced h-BN unit in the amorphous layer compared with top-side h-BN layer. However, the interlayer also exhibits weak Al  $L_{2,3}$  and O  $K$  signals, which are not detected in top h-BN film. This indicates that the sapphire must have somewhat decomposed and diffused into the interfacial layer. Further to explore the effect of growth temperature on sapphire decomposition and interfacial amorphization, the BN layers are grown on sapphire substrate at 1030°C, 1230°C and 1330°C. Looking into the crystal structure by cross-sectional TEM, interfacial amorphization occurs at growth temperature of 1230°C and 1330°C, but the smaller thickness of amorphous interfacial layer for sample grown at temperature of 1230°C is achieved as compared to that grown at 1330°C. Instead, the abrupt interface with no visible amorphous interlayer is observable for sample grown at 1030°C. The results indicate that the generation of amorphous interfacial layer is closely correlated to the growth temperature of h-BN. Some thresholds for the formation of the amorphous interfacial layer seem to have existed, being either dependent on temperature or temperature-related processing conditions. On the basis of these findings, it seems very reasonable to link the interfacial amorphization with sapphire degradation at high temperature, where the amorphous BN interfacial layer could be formed by interdiffusion at h-BN/sapphire interface region due to sapphire degradation at high temperatures. Eventually, a temperature-related formation mechanism for the amorphous interfacial layer at interface is proposed.

On the other hand, the origin of the surface wrinkling in h-BN layers with a large thickness is also elucidated in this work. Morphology development of h-BN layers with different thickness is studied in detail, where the varied film thickness is obtained by varying the growth time (Growth rate is determined from the cross-sectional TEM measurement). Prior to h-BN growth, sapphire wafers are subjected to 3 min thermal cleaning (THC) at temperature of 1330°C. The sapphire surface damage occurs with voids formation but it can be significantly inhibited when reducing THC time from 3 min to 0 min. As growth starts, h-BN exhibits smooth surface in non-damaged area after 1 min growth, indicating the growth is dominated by layer-by-layer mode at initial first few layers deposition. However, it apparently starts to change at ~ 3 min, similar to the Stranksi-Krastanov (S-K) growth mode, where the islands begin to become visible on the surface. Along with the growth time, the small islands increase in size and decrease in density as they merge with each other with increasing the thickness. At a film thickness of around 5 nm, some small pin-holes are observable on film surface, indicating the separation of two h-BN 2D islands that are in the process of coalescing

for larger grains. Meanwhile, the ridge-like features also become observable on the surface and they are mostly located at the coalesced boundary of h-BN islands. Further to grow thicker layers, the individual grains become more difficult to be distinguished and the prominent wrinkled patterns begin to present on h-BN surface. To inspect the structural properties of the wrinkles, the cross-sectional STEM images exhibit the microstructure of local wrinkle. A clear buckling in BN layer appears in the wrinkled area and the stacks of as-grown BN layers is not highly *c*-oriented. Instead, film is less ordered at the maximum height of a wrinkle and a clear grain boundary can be seen, indicating the coalescing for h-BN grains with different orientation likely occurs at the wrinkle region. It suggests that the surface wrinkling of h-BN may take place during growth in this work, despite the belief that surface wrinkling occurs during post-growth cooling in many previous studies. Additionally, in case the wrinkle created by local delamination during cooling process, typically, it would leave a hollow area between delaminated h-BN layer and supported substrate. However, the hollow feature is not found by cross-sectional TEM observation in our study. On the contrary, the area beneath the wrinkle seems filled with some materials, in which the interfacial layer shows a larger thickness against that in non-wrinkled area. To confirm the result, atomic resolution EDX mapping is performed to characterize the element composition in the wrinkled area. It is found that B and N are detected in the wrinkled area, while a larger amount of Al and O are also observable in the interlayer beneath the wrinkle compared with the non-wrinkled area. It has been discussed that the interfacial layer formation is correlated to the sapphire degradation with interdiffusion between h-BN and sapphire, and hence Al and O elements are found in the interfacial layer. Compared with the non-wrinkle area, a stronger signal of Al and O from interfacial layer beneath wrinkle suggests that a stronger reaction occurs there. In fact, it is reasonable to understand the sapphire degradation that may be severe at the wrinkle area. The wrinkles formation is ascribed to the 2D h-BN islands coalescence, where the h-BN grain boundary is produced due to imperfect lateral coalescence. From the viewpoint of kinetics, the grain boundary area can provide a lower barrier for active-species to out-diffusion and in-diffusion, resulting in a thicker interfacial layer with more Al and O inclusion. Furthermore, contribution to formation of the interfacial layer in the wrinkled area with a large thickness is partially attributed to the coalescence process itself between the h-BN islands. Since at the wrinkled area the h-BN islands coalescence proceeding in h-BN grains with different orientation, and hence the imperfect coalescence easily occurs, leading to disordered BN formation. In this case,

the surface wrinkles are mainly ascribed to the imperfect lateral coalescence between h-BN domains rather than the cooling process after growth.

On the basis of the knowledge of growth evolution in h-BN, a growth model of h-BN grown on sapphire is eventually proposed in this research, where monolayer or few monolayers h-BN can be achieved at initial a few growth pulses (<60 cycles), following the layer-by-layer growth mode. At this stage, h-BN does initially nucleate as triangular single-crystal domains. After the first few h-BN layers, the subsequent h-BN nucleate does not form large triangular single-crystal domains any more, but nucleate into nanocrystalline domains overgrowing on the initial smooth 2D h-BN layers. These nanocrystalline domains possibly nucleate at defects or domain edges and eventually formation of small individual circular islands. It is apparent that the average size in nanocrystalline islands (~60 nm) are much smaller than that of the initial single-crystal triangular domains (~600 nm) underlying the small island. The observations indicate that the h-BN grown on sapphire (without any nucleation buffer layer) transits from layer-by-layer growth to S-K mode growth, where island growth becomes favorable to layer-by-layer growth with thickness increase. Albeit further improvement is highly needed to growth of h-BN layers with a large thickness, in this work it has realized to epitaxial growth of atomically flat, wafer-scale and single-crystalline h-BN films by MOCVD with thickness in monolayer or just few monolayers. This would pave the way to achieve high crystal quality h-BN film with desired thickness.

Conventional group-III nitride compounds have been intensively studied and used in various applications. As a member of the III-nitrides, to combination of h-BN with other conventional III-nitrides such as AlN, GaN etc. in MOCVD system will be very attractive. It may not only bring novel device design but also realize *in-situ* integration. Whereas, the study on epitaxial growth of h-BN on III-nitrides by MOCVD is quite scare. The integration of h-BN with other conventional III-nitrides will bring more opportunities for future applications. The h-BN grown on AlN and GaN surface are thus studied in Chapter 5. Particularly, the nucleation of h-BN on AlN is systematically investigated. Large TEB flow rate facilitate h-BN nucleation but significant loss in nuclei size. Small TEB flow can enlarge the nuclei size but is difficult to nucleation at initial stage at high temperature, resulting in a long time for a coalesced h-BN film on surface. Consequently, high temperature and moderate TEB flow is suggested for one-step directly grow h-BN on AlN. On the basis of above findings, single-crystalline h-BN layers were in success grown on AlN surface with uniform

thickness. Interestingly, similar to h-BN grown on sapphire, the almost same wrinkled patterns also appear in h-BN films grown on AlN surface. In the analogue of h-BN grown on sapphire, it has been proved that the surface wrinkling of h-BN grown on AlN template is created during growth with mixed layer-by-layer plus island growth, where a rough lateral merging occurring at many grain boundaries, leading to surface wrinkling takes place. In addition to integration of h-BN with AlN, combination of h-BN with GaN is also attractive for future high performance GaN-based electronic devices. Because of many potential properties, such as wide bandgap, high thermal stability and conductivity, atomically flat surface, ideally without dangling bonds, h-BN as layered material has been used as an insulating layer in 2D heterostructure devices. On the other hand, 3D amorphous oxide and nitride insulating have been commonly employed as gate insulators in many semiconductor electronic devices. There is no exceptional for GaN-based devices if one contains the dielectric film. Besides, high dielectric strength and electrical reliability of h-BN have been reported to be comparable to SiO<sub>2</sub>. To apply h-BN as novel dielectric layer in GaN-based devices is possible to be one of the promising ways to achieve further performance enhancement in device. Particularly, it allows us to *in-situ* growth of device heterostructure in same chamber (MOCVD system) without additional transfer process. This enables to avoid some additional contaminations on interface, which is extremely critical to device performance. Unlike h-BN grown on sapphire and AlN, however, single-crystalline h-BN grown on GaN by MOCVD is still not achieved in this work due to the limitation in available growth temperature. But the dielectric properties of non-crystalline BN film based on both BN/n-GaN and Al<sub>2</sub>O<sub>3</sub>/BN/n-GaN gate stacks are studied. Large leakage current in BN/n-GaN MIS capacitors and increased frequency and hysteresis Al<sub>2</sub>O<sub>3</sub>/BN/n-GaN MIS capacitors requires a further quality improvement in BN dielectric itself and BN/GaN interface. However, C-V characteristic exhibits a large positive shift in flat band voltage in Al<sub>2</sub>O<sub>3</sub>/BN/n-GaN MIS capacitors as compared to Al<sub>2</sub>O<sub>3</sub>/n-GaN MIS capacitors, indicating the potential to fabricate normally-off MISFET by introducing BN layer in gate stacks.

On the basis of the discussions above, the key contributions in this research could be summarized as follows.

Firstly, direct growth of single-crystalline h-BN on sapphire substrates by pulsed-mode MOCVD is successfully demonstrated and obtained. The growth behavior of h-BN grown on sapphire by pulsed-mode MOCVD is systematically studied.

Second, the interfacial amorphization at h-BN/sapphire interface is observed and investigated for the first time, and also a temperature-related mechanism is proposed to account for its formation. Meanwhile, the origin of h-BN surface wrinkling is elucidated in this work and the evolution model of h-BN grown on sapphire is proposed accordingly.

For the first time, direct growth of single-crystalline h-BN layers on AlN surface by MOCVD and systematically investigated the nucleation of h-BN and growth behavior on AlN surface.