Grain Boundary Structure of *c*-BN Thin Film Synthesized by PVD Method

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Microstructure of cubic boron nitride (*c*-BN) films deposited on a Si substrate was investigated by transmission electron microscopy. The presence of cubic phase was clearly confirmed by taking the microdiffraction pattern and lattice image. Hexagonal boron nitride (*h*-BN) with thickness 1-2 nm was often observed at the boundaries of *c*-BN films. The *h*-BN phase at the boundary of the *c*-BN may be the reason of the high intrinsic compressive stress. It was suggested that the *c*-BN phase nucleated on the prism plane of *h*-BN keeping the parallelism between the (111) *c*-BN and (0001) *h*-BN, although the slight deviation ($\sim 4^\circ$) was observed in some cases. The nucleation mechanism of *c*-BN was discussed analogous to that of diamond on graphite.

Keywords: cubic boron nitride, hexagonal boron nitride, thin film, high resolution electron microscopy, ion-plating method, orientation relationship

I. Introduction

Cubic boron nitride (*c*-BN) has been intensively studied for its extreme hardness next to the diamond. The *c*-BN film is not only a candidate for cutting tools utilizing the mechanical properties but also for electronic device due to its wide band gap⁽¹⁾. The grain size of PVD *c*-BN is extremely small, 5-20 nm, and therefore conventional scanning electron microscopy does not offer useful information on the microstructure of the films. The structure of *c*-BN thin films have been studied for several years mainly using Fourier transformation infrared (FTIR) spectroscopy⁽²⁾.

It has been pointed out that *c*-BN thin films have higher stress than any other films⁽³⁾. We suppose that it attributes to the grain boundary structure at which misfit between two grains would produce certain strain. In this paper, we first show clear evidence of well-crystallized *c*-BN films through high resolution electron microscopy (HREM) and the microdiffraction method. Second, Grain boundaries of *c*-BN are observed to investigate the origin of higher compressive stress in the *c*-BN films. Finally, the orientation relationship between *c*-BN and *h*-BN will be directly shown and discussed analogous to diamond on graphite

II. Experimental

The films for electron microscopic observation were

synthesized on a Si(111) substrate at 400°C by ion-plating method⁽⁴⁾⁻⁽⁷⁾. Before the *c*-BN deposition, Ti was first coated on a Si (111) substrate as an intermediate layer and second, a boron-rich amorphous layer was deposited to improve the adhesion strength. Finally, stoichiometric *c*-BN was grown to about 200nm thick. HREM was performed on TOPCON EM 002B operating at 200kv, equipped with Philips 9900 energy dispersive X-ray analysis (EDS). Fast Fourier transformation (FFT) for analyzing the HREM image was carried using LUZEX III image process in order to investigate the crystallographic information. The plan-view sample was prepared by peeling the film from a Si substrate and then following by backside ion thinning. The cross-sectional specimen was prepared by conventional method⁽⁸⁾.

III. Results and Discussion

III. 1. Identification of *c*-BN phase

Most study on *c*-BN thin film have used FTIR spectroscopy for phase identification because the cubic phase has an absorption peak at $\sim 1080\text{cm}^{-1}$ which the hexagonal and amorphous phases each have primary and secondary absorption peak at 1370 and 780cm^{-1} , respectively. It is noted that the absorption peak at $\sim 1080\text{cm}^{-1}$ only suggests the presence of sp^3 coordination and does not give crystallographic information⁽⁹⁾⁽¹⁰⁾. Thus in order to obtain the crystallographic information, the diffraction method should be necessary.

Fig.1 [110] microdiffraction pattern of c-BN.

Fig.2 A low magnification of Cross-sectional thin film.

Figure 1 is a microdiffraction pattern from a single grain of *c*-BN taken along the [110] direction by focusing the electron beam to $\sim 20\text{\AA}$. Four strong 111 and two 220 are clearly seen, together with two weak 200 reflections, since the structure factor of {200} of *c*-BN is much smaller than that of {111} and {220} of *c*-BN. By measuring the angle between the {111} planes and the distance between transmitted beam and reflected beam from the {111} planes, it was confirmed that the diffraction came from one of the *c*-BN grains. Figure 2 is low magnification cross-sectional transmission electron micrograph of the specimen used in this experiment. A *h*-BN layer, $\sim 0.05\text{ }\mu\text{m}$ thick appears between the *c*-BN and amorphous BN layer. The result of Figure 2 indicate that sequential layers of *a*-BN and *h*-BN were the sources of noncubic phases that have been detected by FTIR. It is confirmed that the *c*-BN, *h*-BN and *a*-BN phases are clearly separated from each other.

III. 2. Grain boundary of c-BN

Figure 3 is a plan-view HREM micrograph of *c*-BN

Fig.3 A plan-view HREM image of *c*-BN, indicating that moiré-like fringes appear on the boundaries denoted by R, S and T.

Fig.4(a) Simulation of moiré pattern, (b) Two (111) lattice M and N overlap to form two orientational fringes denoted by H and L.

films. The planar defects are seen inside the grains with 10–20 nm in size. It is noted that moiré-like fringes are seen at the grain boundaries of *c*-BN as indicated by S and R. If they are moiré pattern, the direction of fringes should be unique as shown in Figure 4(a)⁽¹¹⁾. However, the fringes observed in this experiment had two different direction as indicated by H and L as shown in Figure 4(b). Further, the simulated spacing was 2.78 Å, but the observed spacing was 3.3 Å which agreed with that of the (0002) plane of *h*-BN. Thus, it is concluded that these fringes attribute to the

Fig.5 Triple junction of *c*-BN grains. Inset is FFT result of triple junction area.

Fig.6 Cross-sectional view shows that between *c*-BN grains O and P *h*-BN exists. Inset is FFT of the boundary area.

lattice image from the (0002) *h*-BN. Another evidence which indicated the presence of (0002) plane is shown in Figure 5. The fringe at the triple junction has one direction, although the junction is surrounded by three grains with different directions. A Fast Fourier Transformation of the lattice among the triple junction was shown in the inset. The two strong diffraction spots are coincident with the (0002) *h*-BN and (111) *c*-BN, respectively.

Cross-sectional observation in upper part of the film also indicated the presence of *h*-BN phase at the boundary of *c*-BN as shown in Figure 6. Between two sets of *c*-BN grain, denoted as O and P, there are lattice fringes at the boundaries. Here, the interplanar spacing of fringes was also ~0.33 nm and identical to that of (0002) *h*-BN. The FFT of the image indicated that the diffraction spots corresponded to the (111) *c*-BN and (0002) *h*-BN, respectively.

In a brief summary, there is no species which effectively etch non-cubic phases in the synthesis of *c*-BN films. Thus, it is considered that the grain boundaries are formed when the non-cubic phases are accidentally deposited on *c*-BN grains. The deposition of non-cubic phase may continue until the cubic phase is deposited. Eventually, *c*-BN films which contains slight amount of *h*-BN phase would be formed as schematically shown in Figure 7. This might be the reason for generating strong intrinsic compressive stress.

Fig.7 Schematic of *c*-BN thin film. *h*-BN phase exists on the boundaries of *c*-BN

III.3. Orientation relationship between *h*-BN and *c*-BN

Figure 8 is a HREM photograph of *c*-BN grains taken from [110] direction, where the lattice image from $(\bar{1}\bar{1}1)$ and $(1\bar{1}\bar{1})$ are seen. Inside the *c*-BN grain, the microtwins are clearly observed. The *h*-BN phase with thickness about 1–2 nm is seen along the *c*-BN grain boundaries. In the A and B areas, the {0002} *h*-BN are seen as fringes contrast

with 0.33nm. Since the {0002} planes are bounded through π electrons, the fringes contrast is not straight but a little bit

Fig.8 A plan-view HREM image of orientational relationship between *c*-BN and *h*-BN.

Fig.9 A HREM image of initial stage growth of *c*-BN. Note *h*-BN (0002) // *c*-BN (111), but a few degree deviation.

curved and rotated analogous to the turbostratic carbon. However, looking carefully at the edge of {0002} fringes, they are continuously connected to the {111} plane of *c*-BN phase. In the area A and B, the (0002) planes are parallel to the (111) and (111) planes, respectively.

It has been reported that *h*-BN is first deposited before *c*-BN grew on top of it by observing cross-sectional specimen. Figure 9 is a cross-sectional HREM photograph of *c*-BN films at the initial stage of deposition, that is, the observed area is closed to the Si substrate. The purpose of this investigation is to confirm that *h*-BN which was deposited at the initial stage of deposition also have similar orientation relationships to those of Fig.8. It is noted that the {0002} and {111} planes in D and E area are almost parallel, but in the F area, the slight deviation by several degree are seen.

Thus, it is thought that an unique orientation relationship exists in this system, which is similar to the case of diamond on graphite⁽¹²⁾⁻⁽¹⁵⁾, as follows

$$(0001)h\text{-BN} \parallel (111)c\text{-BN} \text{ and } \langle 11\bar{2}0 \rangle h\text{-BN} \parallel \langle 110 \rangle c\text{-BN}$$

Although we have not observed the second relationship in the film, the parallelism has reported in the specimens synthesized at high pressure and high temperature⁽¹⁶⁾⁽¹⁷⁾. We think a few degree deviation is attributed to the geometrical arrangement or misfit at the interface between the (0001) *h*-BN and (111) *c*-BN planes.

IV. Conclusion

Microstructure of *c*-BN films synthesized by the ion-plating method were observed and characterized by high resolution electron microscopy and microdiffraction method. The following results were obtained.

(a) Lattice image taken along the [110] direction showed that *c*-BN film was well crystallized with an interplanar distance of $\sim 2.1\text{\AA}$, although the grain size was extremely small, from 5 to 20 nm.

(b) The microdiffraction pattern along the [110] direction by focusing the electron beam to $\sim 20\text{\AA}$, clearly showed that the small grains were consisted of single crystal *c*-BN.

(c) Thin layer of hexagonal boron nitride (*h*-BN) phases were often observed at the boundaries of *c*-BN grains. The observed interplanar spacing was 0.33nm and coincided with that of the (0002) plane of *h*-BN.

(d) The existence of *h*-BN on the grain boundaries of *c*-BN may be the reason to generate the compressive stress and microcracks in *c*-BN thin films.

(e) It was suggested that *c*-BN was nucleated on the prism plane of *h*-BN, keeping the parallelism of (0001)*h*-BN // (111)*c*-BN

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