Boron Nitride Films Grown by Low Energy Ion Beam Assisted Deposition

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Boron nitride films were synthesized with N_2 ion flux of low energy, up to 100 eV, at different substrate temperatures of no heating, 200, 400, 500, and 800°C, respectively. Boron was supplied by e-beam evaporation at the rate of 1.5 Å/sec. For all the conditions, hexagonal BN (h-BN) phase was mainly synthesized and high resolution transmission electron microscopy (HRTEM) showed that (002) planes of h-BN phase were aligned vertical to the Si substrate. The maximum alignment occurred around 400°C. In addition to major h-BN phase, transmission electron diffraction (TED) rings identified the formation of cubic BN (c-BN) phase. But HRTEM showed no distinct and continuous c-BN layer. These results suggest that c-BN phase may form in a scattered form even when h-BN phase is mainly synthesized under small momentum transfer by bombarding ions, which are not reconciled with the macro compressive stress model for the c-BN formation.

Key words: c-BN, h-BN, Ion beam assisted deposition

I. Introduction

Boron nitride (BN) is one of the most interesting material from technical and scientific viewpoint. Especially cubic boron nitride has excellent properties of extreme hardness, chemical inertness and it has attracted much attention as industrial applications.

Concerning the synthesizing mechanism, ion bombarding has been considered to be crucial for forming cubic boron nitride, regardless with the deposition method. Mckenzie[1,2] *et al.* note that ion bombarding creates compressive stress and that c-BN forms only if the compressive stress exceeds a critical value. He assumed that macro bi-axial stress evolved in films caused a thermodynamic phase transition of h-BN to a denser form of c-BN. They showed a stress evolution of h-BN with film thickness in which the stress was small for very thin films, but increased rapidly with thickness, reached a maximum, and then fell. The phase transition from h-BN to c-BN should occur at certain thickness over the whole layer due to the macro bi-axial stress. From the equilibrium thermodynamic analysis of the Gibbs free energy in a bi-axial stress field, about 1.5 GPa was proposed as a minimum stress for c-BN formation.

Experimentally Kester[3] suggested a threshold value of momentum transfer per atom of 200 $(eV \times amu)^{1/2}$ above which films were cubic and once the growth of cubic phase was initiated, the layer had no h-BN phase. Even no grain boundary region was observed. Such threshold value of momentum transfer for c-BN formation have been considered to need to create the compressive stress in growing films which was suggested by Mckenzie *et al.*[1,2] for c-BN formation.

On the other hand Robertson[5] proposed a subplantation model for c-BN formation. Ions subplanted below the surface increase the local density and the atomic hybridization state in local area may be adjusted to suit the local density, sp^2 for low density or sp^3 for high density. The crystallization was considered as an by-product from the hetero-polar bond property of BN compound.

In stress point of view, subplantation might be regarded as a means of generating the stress. But Robertson's subplantation model assumes no macro stress in the layer and c-BN formation occurs at very localized area in such manner that cannot be described by the thermodynamic transformation. The c-BN formation due to the local density increase may require less severe ion bombarding condition than that for the critical macro bi-axial stress. In addition, the transition from h-BN to c-BN phase don't have to be abrupt and c-BN phase need not form a continuous layer in subplantation model. Freudenstein *et al.*[4] also argued that h-BN to c-BN transition is not abrupt but rather gradual. They suggested that c-BN takes place over the film once the conditions for c-BN formation are reached. Nevertheless, some h-BN still continues to grow but is gradually displaced by c-BN in phase.

Considering that the stress has been considered to be essential for the c-BN formation, obtaining c-BN films with low stress seems to be limited by the formation mechanisms themselves. Most c-BN films have been reported to have a large compressive stress in the GPa range. The compressive stress remaining in c-BN films has been reported to become smaller for the higher ion energy process: several decades

GPa for <200 eV and less than 5 GPa for >1000 eV ion energies.[6]

Such a large stress is a major problem of c-BN deposition in view of future industrial applications. The compressive stress inevitably limits the amount of film that can be deposited without peeling off. Around 4000 Å is now considered as a maximum thickness of c-BN without peeling off.[7,8] Thus the reducing the stress is a key for the deposition of thick c-BN films for their applications. In order to reduce the residual stress in c-BN films, we should see if macro compressive stress is essential for the c-BN formation.

In this research, we synthesized boron nitride films with ions of low energy which seems to be difficult to generate macro stress enough for c-BN formation. No argon was added for preventing further bombarding effect. And we examined whether c-BN phase was formed and the transition from h-BN to c-BN was abrupt or not. We also examined the microstructure of them. The phase identification was carried out with fourier transform infra-red (FTIR), transmission electron diffraction (TED), and high resolution transmission electron microscopy (HRTEM) and the stoichiometry was confirmed with auger electron spectroscopy (AES).

II. Experimental Procedure

The BN films were deposited using a ion beam assisted deposition system which was equipped with a electron beam evaporator and a end hall type ion gun. The electron beam evaporator is equipped with a 10 kW(10 kV, 1A) electron gun and the capacity of the hearth is 30 cc. Boron was evaporated at the rate of 1.5 Å/sec. Pure(>99.999%) nitrogen gas without argon was ionized by the end-hall type ion gun whose maximum ion current and energy were approximately 1 A and 100 eV, respectively. The distance between ion gun and the substrate was about 35 cm and the incidence angle of ion beam to the substrate normal was about 25°. The ion energy was varied into 60, 80, and 100 eV, respectively and the ion current was 400 mA which produced approximate 91 μA/cm² of the current density at the substrate. The substrate was heated at 200°C, 400°C, 500°C, and 800°C, respectively, by SiC heater located at back side of the substrate. The film thickness was in-situ estimated via a quartz sensor and the thickness ranged from 1300 to 2000 Å.

The BN stoichiometry was confirmed by AES and the synthesized BN phase was identified with FTIR and TEM. FTIR spectra were obtained from 500 cm^{-1} to 4000 cm^{-1}.

III. Results and Discussion

BN films were synthesized with different ion energies of 60, 80, and 100 eV, respectively. The substrate temperature was 400°C. Fig. 1 shows the depth profile of the elements on the h-BN film grown at 100 eV ion energy. The composition of boron and nitrogen were approximately 52% and 46%,
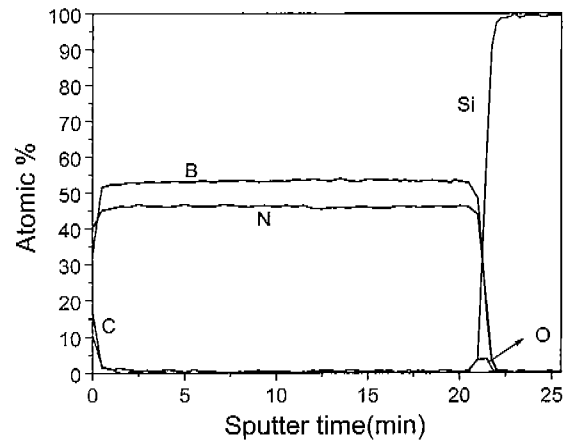

Fig. 1. AES depth profile of the BN film grown on Si(100) under following conditions: N$_2$ ion energy: 100 eV, boron evaporation rate: 1.5 Å/sec, substrate temperature: 400°C.
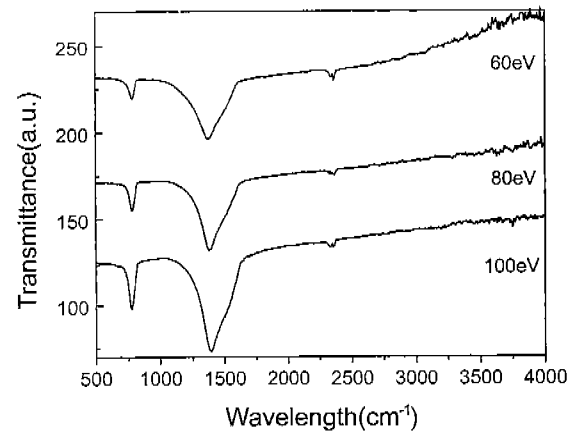

Fig. 2. FTIR spectra of BN films grown with various nitrogen ion energies of 60 eV, 80 eV, and 100 eV respectively. All the films are deposited on Si(100) substrates under following conditions: boron evaporation rate: 1.5 Å/sec, N$_2$ ion bombarding, substrate temperature: 400°C.

respectively, indicating a nearly stoichiometric value. Wada[8] reported a similar AES result for a stoichiometric BN film.

Fig. 2 shows FTIR spectra for the h-BN films grown at 60 eV, 80 eV, and 100 eV ion energy, respectively. The film showed two distinct absorption IR peaks of 780 cm^{-1} and 1380 cm^{-1} which corresponded to out of plane B-N-B deformation mode δ_{op} and in plane B-N stretching mode v_{ip} in (002) plane of h-BN phase, respectively. No absorption peak for c-BN(1080 cm^{-1}) was observed. Thus h-BN phase was mainly synthesized under these conditions.

The ratio of the heights of h-BN v_{ip} and δ_{op} peaks, $R_{v\delta}(=A_{v_{ip}}/A_{\delta_{op}})$, was different with ion energies. $R_{v\delta}$ represents the orientation of h-BN (002) planes with respect to the substrate surface. For the normal incidence of unpolarized IR to the surface, $R_{v\delta}$ will have smaller value as (002) planes of h-BN phase align to be vertical to the surface.[9] With increasing ion energies up to 100 eV, $R_{v\delta}$ decreased as follows: 2.8 for 60 eV, 2.45 for 80 eV, and 2.0 for 100 eV. This meant that more
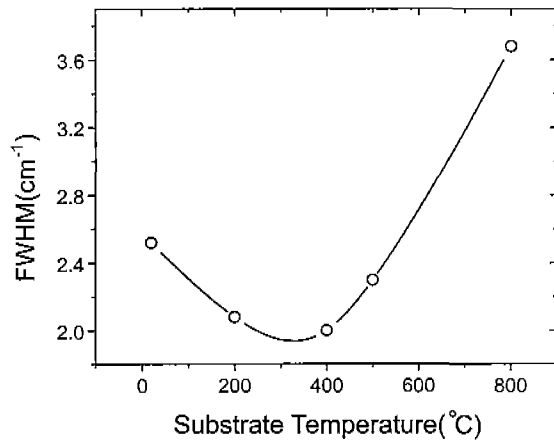
Fig. 3. $R_{v8}(=A_{v8}/A_{\delta op})$ ratio of BN films grown at various substrate temperatures of no heating, 200°C, 400°C, 500°C and 800°C, respectively. All the films are deposited on Si(100) substrates under following conditions: boron evaporation rate: 1.5 Å/sec, N_2 ion energy: 100 eV.

(002) h-BN planes aligned to be vertical to the surface with higher ion energies. This trend can be understood from the viewpoint of macro stress evolved in the film during growth. As the ion energy increases up to 100 eV, the compressive stress in BN films have reported to increase.[10] The elastic property of h-BN phase is anisotropic and (002) planes aligned to be vertical to the stress plane are energetically favorable.

Fixing the ion energy at 100 eV, substrate temperatures were changed into no heating, 200°C, 400°C, 500°C and 800°C, respectively. All the films showed the distinct h-BN IR peaks and the R_{v8} ratio showed a systematic variation with substrate temperatures. As shown in Fig. 3, the R_{v8} decreased at first and then increased with substrate temperatures. Intermediate temperature of around 400°C showed better alignment of h-BN (002) planes than higher or lower temperatures.

To confirm the alignment of h-BN (002) planes, cross sectional HRTEM observation of the BN films synthesized at 400°C and 800°C was carried out. Fig. 4 shows HRTEM image of the BN film synthesized at 400°C. Fringes represent h-BN (002) planes whose spacing is about 3.3 Å. Amorphous/randomly oriented h-BN phases (a-BN) are grown first just above the silicon substrate. And then oriented h-BN layer is formed. Such sequence of phase evolution is well agreed with previous results.[11] Comparing with the HRTEM image of the BN film synthesized at 800°C(Fig. 7), it is easily noticed that (002) planes of the film synthesized at 400°C align more than those at 800°C.

Different alignment of h-BN (002) planes with temperatures was supposed to be explained from the temperature dependency of atomic diffusivity. As temperature increases the atomic diffusivity increases, which have two different (contrary) effects on the alignment of (002) planes. The more mobile the atoms, the faster the alignment proceeds but the less efficient the initial stress evolution by ion bom-
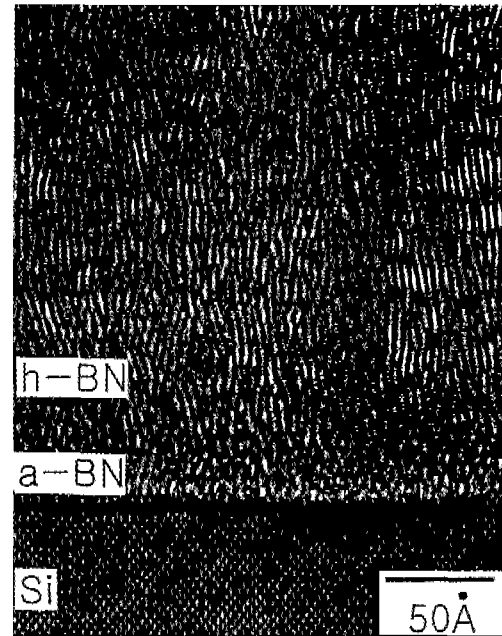

Fig. 4. HRTEM image of BN film grown on Si(100) under following conditions: N_2 ion energy: 100 eV, boron evaporation rate: 1.5 Å/sec, substrate temperature: 400°C.

barding. At much lower temperature, the kinetics for the alignment is too slow and, at much higher temperature, the driving force for the alignment is too small. Thus at intermediate temperature we can see the best alignment. Such alignment of h-BN (002) planes due to the compressive stress seems to be well described by the classical thermodynamics and is reconciled with Mckenzie's macro stress model.

Focused interest in this research was whether c-BN phase might be synthesized even at low ion energy and flux conditions where the evolving macro stress was supposed to be small. We could observed a small peak around 1080 cm^{-1} (arrow indicated) for c-BN only for the BN film synthesized at 800°C(Fig. 5). To verify the c-BN peak in 800°C specimen, cross sectional TEM observation was carried out. Fig. 6
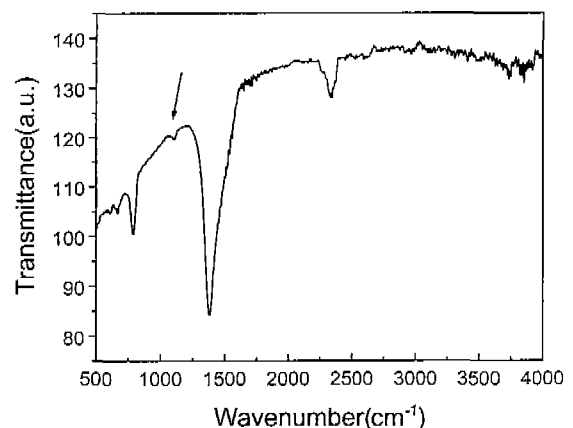

Fig. 5. A FTIR spectrum of BN film grown on Si(100) under following conditions: N_2 ion energy: 100 eV, boron evaporation rate: 1.5 Å/sec, substrate temperature: 800°C.

Fig. 6. A TED pattern of BN film grown on Si(100) under following conditions: N_2 ion energy: 100 eV, boron evaporation rate: 1.5 Å/sec, substrate temperature: 800°C.

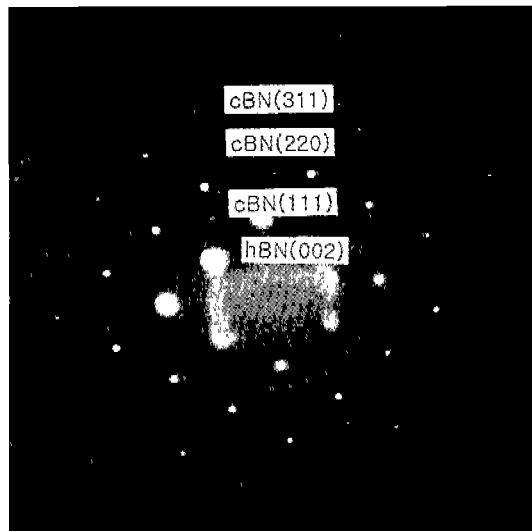

Fig. 7. HRTEM image of BN film grown on Si(100) under following conditions: N_2 ion energy: 100 eV, boron evaporation rate: 1.5 Å/sec, substrate temperature: 800°C.

shows the TED pattern including the Si substrate and whole thickness of the BN layer. The background spot patterns are for the Si substrate. The spot shape represents the direction of e-beam is [110]. Four diffraction patterns are identified as BN phases. The first diffraction is not a full circle but a symmetric small arc, which is identified as (002) planes of h-BN phase. Such small arc patterns represent oriented h-BN layer. Comparing with the spot patterns for Si substrate, we know that (002) planes of oriented h-BN phase are vertical to the silicon substrate surface. In HRTEM(Fig. 7), oriented h-BN layer can be found and such orientation relation was confirmed.

Due to the similar plane spacings, diffraction rings from the second to the fourth may be identified as both diffractions from (111), (220), and (311) planes of c-BN phase and/or from (100), (110), and (200) planes of h-BN phase, respectively. Diffraction patterns from h-BN phase should be arc like the first TED pattern for (002) planes because h-BN phase is well aligned. But from the second to the fourth patterns have the shape of entire rings rather arcs, thus we distinguished them from diffractions from only h-BN phase and we concluded that they represented the formation of c-BN phase. (The brightness of the rings are not uniform. The brighter sections exist at an angle of 90 degrees with the (002) diffraction arcs. Such brighter section of the rings are supposed to have its origin in aligned (100) and (110) planes of h-BN phase.)

In HRTEM image over the whole thickness of the film, we could not find a continuous layer of c-BN and even localized c-BN fringes. They seemed to scatter over the layer in small sizes in random orientation. This result conflicts with Kester's report. Kester argued that once the growth of c-BN phase initiated, the layer was single phase. Such understanding has the basis of the growth mechanism of macro compressive stress in plane. The macro stress model by Mckenzie hardly explains the coexistence of c-BN and h-BN
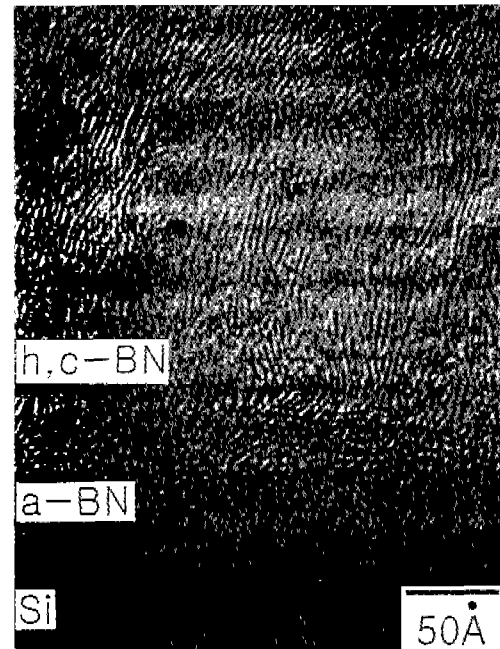
phase in a layer. They think the only possible origin of h-BN is the initial layer and at certain thickness where the critical stress for forming c-BN is generated c-BN phase starts to form over the whole layer.

The fact that c-BN phase is formed at high temperature of 800°C and low ion energy of 100 eV arises a question to a macro stress model for c-BN formation. The boron evaporation rate of 1.5 Å/sec, the ion energy of 100 eV, and the ion current density of 91 µA/cm² make about 19.4 (eV×amu)^{1/2} which is much smaller than the threshold momentum transfer of 200 (eVq×amu)^{1/2} for the c-BN phase formation suggested by Kester *et al.*[3] Thus the growth condition in this research dose not seem to be enough to create the macro stress over the whole layer for the formation of c-BN phase.

When energetic ions bombard the surface, it does not seem to be the only possible way to form a phase in a classical thermodynamic manner where macro stress is built up over the whole layer. We should note that rather very localized ion beam bombarding effect may act as a important role for the phase evolution in ion involved processes. The formation of c-BN phase in this research, which is not a continuous layer but in a scattered from, is possibly explained by the local ion bombarding effect. Regardless the macro stress in the film, local stress can be generated by ion bombarding,[12] which affect the hybridization state of atoms, and the very restricted region can be formed into c-BN phase.

IV. Conclusions

Aligned h-BN phase was mainly synthesized by ion beam assisted deposition method using ions of small energies up

to 100eV. The best alignment was observed at intermediate temperature of around 400°C. Such alignment of h-BN (002) planes was able to be explained by the compressive stress which might be evolved during the growth. Cross sectional TEM observation proposed that c-BN phase formed in a scattered form even when h-BN phase was mainly synthesized under small momentum transfer by bombarding ions. This observation dose not seem to be appropriately explained by the macro stress model where they assume a phase transition at a critical macro stress from the point of view of classical thermodynamics. The local effect of ion bombarding is supposed to suit for understanding the c-BN formation in this research.

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