Preparation and internal stress estimation of BN films by ion mixing and vapour deposition technique

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Abstract. Boron Nitride (BN) films were synthesized onto silicone wafer by depositing B metal vapour under simultaneous irradiation of N ions. Here, film thickness, ion beam energy and transport ratio ($B/N$) were selected as a preparation parameter and they were controlled in the range of 0.2-1 $\mu$m, 0.2-2keV and 1-5, respectively. The BN films prepared were characterized using several analytical techniques and their internal stresses were estimated using Stoney’s equation. From Fourier transform infrared spectroscopy, it was found that use of low energy N ions is effective for the formation of cubic BN (cBN) phase using ion mixing and vapour deposition (IVD) technique. At this condition, high compressive stress is measured and strong correlations were found among crystal structure, internal stress and Knoop hardness of BN films.

1. Introduction
Boron nitride (BN) film has excellent properties such as high hardness, thermal conductivity, thermal stability and so forth [1]. It is very difficult, however, to synthesize the cubic BN (cBN) phase because it is a metastable phase under atmospheric pressure like a diamond. It has been widely recognized that the successful formation of cBN phase requires a bombardment of growing films with energetic ions [2,3,4]. This intensive ion bombardment also produces high compressive stress in the film [4,5,6]. In nucleation and growth of cBN film, however, full understanding of the mechanism has not been established yet. The purpose of this study is to clarify the effects of processing parameters on the internal stress of BN films prepared by ion mixing and vapour deposition (IVD) technique. BN films were synthesized onto silicone wafer by depositing B metal vapour under simultaneous irradiation of N ions. The film thickness, transport ratio ($B/N$) and ion beam energy were selected as preparation parameters [7]. The internal stress of obtained films was also estimated by Stoney’s equation using the Newton ring method and the correlation between crystal structure of BN film and these processing parameters were discussed.

2. Experimental procedure
Synthesis of the BN films was performed using an IVD machine equipped with two bucket-type ion sources, two evaporators and a pumping system. The BN films were synthesized onto silicon (100) wafer and glass substrate (18"x18"x0.12"mm) by depositing B metal vapour under simultaneous irradiation of N ions. The processing parameters for sputter cleaning and film deposition were summarized in table 1.
Table 1. Conditions of sputter cleaning and film deposition.

| Parameter                  | Sputter cleaning | Film deposition |
|----------------------------|------------------|-----------------|
| Acceleration voltage \((E)\) | 5keV             | 0.2~2keV        |
| Acceleration current       | 20mA             | 9mA             |
| Arc voltage                | 80V              |                 |
| Deceleration voltage       | 1.5keV           |                 |
| Ion incident angle         | 45°              | 0°              |
| Transport ratio \((B/N)\)  | 1~5              |                 |
| Film thickness \((d)\)     | 0.2~1µm          |                 |
| \(N_2\) gas flow rate      | 4sccm            |                 |
| Substrate temperature      | N.T.*            |                 |
| Substrate rotation speed   | 0.1rev/s         |                 |

* Normal (intentionally 'no-heated') temperature

Internal stress of BN films was evaluated using the Newton ring method [8]. The Newton rings were measured with an optical microscope equipped with a Michelson interferometer that allows determining the radius of curvature of the substrate \(R\). The internal stress \(\sigma\) was estimated using Stoney’s equation [8] as shown in eq.(1).

\[
\sigma = \frac{E_s h_s^2}{6(1-\nu)Rd}
\]

Here, \(E_s\) and \(\nu\) are elastic modulus and Poisson ratio of substrate, \(h_s\) and \(d\) are thickness of substrate and film, respectively.

The appearance of film surface and cross section was examined by field emission type scanning electron microscope (FE-SEM). Fourier transform infrared spectrometer was also used to determine the crystal structure. The Knoop hardness of BN film on silicon wafer was also measured.

3. Results and discussions

3.1 Morphology and structure

Figure 1 shows examples of FE-SEM micrographs of 1µm-thick BN films prepared at the acceleration voltage \(E=0.2, 2\)keV and the transport ratio \(B/N=4\). All BN films prepared under various conditions were of satisfactory quality with very smooth surfaces. From the SEM observations, it became clear that the BN films exhibited the columnar structure with grainy appearance, less independent of acceleration voltage and/or transport ratio.

Figure 2 summarizes FT-IR spectra of 1µm-thick BN films prepared at transport ratio \(B/N=4\) as a function of acceleration voltage \(E\). For the stoichiometric of BN film at 2keV, only two intensive absorption bands around 1380 and 780 cm\(^{-1}\) were observed. They are assigned to in-plane and out-of-plane vibrational modes of hBN, respectively. However, as the acceleration voltage is decreased, another absorption band can be observed around 1080 cm\(^{-1}\), which can be assigned to the presence of cBN phase [3]. This suggests that low acceleration energy of N ions is effective for the synthesis of cBN films by IVD technique.

3.2 Internal stress of BN film

Figure 3 shows the relationship between internal stress and film thickness of BN films prepared at the acceleration voltage \(E=0.2, 2\)keV and the transport ratio \(B/N=4\). From figure 3, it is confirmed that the compressive stress increases linearly with the increase of film thickness. Besides, the compressive stress tends to become larger at \(E=0.2\)keV in comparison with \(E=2\)keV. This suggests that the compressive stress increase at low acceleration voltage. It is known that internal stress normally increase at high acceleration voltage due to high impact energy of accelerated ions. However, obtained result does not agree with such tendency and it is considered that the increase of internal stress is
related to generation of cBN phase. Figure 4 shows the relationship between internal stress and acceleration voltage of 1\,\mu m-thick BN films prepared at the transport ratio $B/N=4$. From figure 4, it is also confirmed that the compressive stress increases at the acceleration voltage $E=0.2\,\text{keV}$, which can be assigned to the condition for formation of cBN phase.

![Figure 1. FE-SEM micrographs showing surface and cross-sectional views of BN films prepared at acceleration voltage $E=(a,b)0.2\,\text{keV}$ and (c,d)2\,\text{keV} ($B/N=4$).](image)

![Figure 2. FT-IR spectra of BN films prepared at transport ratio $B/N=4$ ($d=1\,\mu m$).](image)

![Figure 3. Relationship between internal stress and film thickness of BN films prepared ($B/N=4$).](image)

![Figure 4. Relationship between internal stress and acceleration voltage of BN films prepared ($B/N=4$, $d=1.0\,\mu m$), data points marked (*) represent specimens that were subjected to hardness testing.](image)

Figure 5 shows the relationship between internal stress and transport ratio of 1\,\mu m-thick BN films prepared at the acceleration voltage $E=0.2\,\text{keV}$. It is confirmed that the compressive stress increases at transport ratio $B/N=4$. It is also confirmed that the mixture phase of hBN and cBN has been formed at this condition [7]. Therefore, it is concluded that the compressive stress of film increases with the
increase of cBN content. The high compressive stress is considered to be caused by transition of crystal structure from graphite type hBN to cBN during film growth. However, there is no experimental evidence and further investigations are required for direct evidence.

Figure 6 shows the relationship between internal stress and Knoop hardness of BN films. Knoop hardness was measured for the specimens which have (*) in figure 4 and 5. The solid line in figure 6 is obtained by least-squares method. The coefficient of correlation is -0.843 and it is confirmed that there is a high correlation between internal stress and Knoop hardness. From these results, strong correlations were found among crystal structure, internal stress and Knoop hardness of BN films.

4. Conclusions
BN films were prepared by IVD technique and internal stress was measured by the Newton ring method. The effect of processing parameters on the internal stress of BN film can be summarized with the following remarks;
(1) Low acceleration voltage of N ions is effective for the formation of cBN phase.
(2) Compressive stress of BN film increases at the condition which cBN phase is formed.
(3) Strong correlations can be found among crystal structure, internal stress and Knoop hardness of BN films.

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