Method for simulating the thickness distribution of a cubic boron nitride film deposited on a curved substrate using ion-beam-assisted vapor deposition

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Abstract

A method for simulating the thickness distribution of cubic boron nitride (cBN) films deposited on a curved substrate using ion-beam-assisted vapor deposition (IBAD) is established and discussed. The deposition conditions are (i) boron arriving rate is 3.2 Å/s, (ii) ion current density is in the range 600–1600 μA/cm², and (iii) gas composition fed into the ion source is 36% N₂ + Ar. It was found that, due to simultaneous deposition and sputtering, the boron resputtering yield (which depends on the ion incident angle during cBN deposition) estimated from experimental data was higher than that of the boron sputtering yield of the BN films with a density of 3.482 g/cm³ calculated by the TRIM code. Using the above empirical boron resputtering yield, it is estimated that in the case of static coating, cBN films would not be formed when the incident angle is more than 40°. However, with continuous waving, the distribution of film thickness improves and the results are consistent with the experimental results. This estimation also agrees with the experimental results of discrete waving deposition within an allowable margin of error.

1. Introduction

Recently, deposition of boron nitride, carbon nitride, silicon nitride, and aluminum nitride films has been conducted using the ion-beam-assisted vapor deposition (IBAD) method, which has several advantages [1]. First, adhesion between the film and the substrate can be improved by removing absorbed contaminant species from the substrate surface and by intermingling deposited atoms and substrate atoms. Second, control of ion species, ion...
energy, and ion flux can each be achieved independently over a wide range. Because of these advantages, new artificial materials like cubic boron nitride (cBN) [2]-[7], diamond-like carbon (DLC) [8]-[11], and C$_3$N$_4$ [12][13], which provide amassing properties, have been developed. These materials are expected to be applied not only to electrical devices but also to mechanical components in various fields. However, because the ion beam is unidirectional, it is more difficult to deposit films on curved surfaces using IBAD than by using chemical vapor deposition or the ion-plating method, and a few existing papers do discuss this point.

Determining the thickness distribution of a thin film deposited on a curved surface by using only the vapor deposition method without ion bombardment may be a matter of simple geometry calculations, where the thickness distribution is influenced by the incident angle ($\theta$) as $\cos \theta$. In the case of IBAD, however, resputtering of films occurs by ion irradiation, thereby complicating the process of determining the thickness. Sueda et al. [12] have experimentally shown that BN films can be deposited by IBAD by waving the substrate, and have suggested that cBN films can be deposited on a curved or sloped surface by waving or rotating. Because a high ion-to-atom-arrival ratio is required for the formation of cBN, the effect of resputtering has to be considered in order to estimate the thickness distribution of the cBN film.

In this study, a method for simulating the thickness distribution of a cBN film deposited on a curved surface using IBAD and the above-mentioned waving process will be developed and discussed by comparing calculated results with experimental results.

2. Method

In most cases in which the cBN films were successfully obtained by the IBAD method, a mixture of nitrogen and novel ions was irradiated on a substrate concurrently with boron deposition [2]-[7]. In the following discussion, it is assumed that a mixture of nitrogen and argon ions is irradiated with boron deposition. The incorporation rate of boron $Q_B$ is

\[
Q_B = \alpha_B F_B - \sum_{k=Ar,N} S_k F_k
\]

where $\alpha_B$ is an initial sticking probability, $F_B$ is the boron arrival rate, $\alpha_B S_B$ is the resputter yield of boron by argon ions, $\alpha_B S_B$ is the resputter yield of boron by nitrogen ions, $F_{Ar}$ is the argon ion arrival rate, and $F_N$ is the nitrogen ion arrival rate. We need to consider the reaction of boron and nitrogen, both on and beneath the film surface, caused by chemical in nature, bombardment-induced and ion implantation. According to many reports [2], [6],[13]-[15], the cBN films were nearly stoichiometric.

In discussing the deposition rate of the cBN films, only the incorporation rate of boron needs to be considered, assuming N/B = 1. A boron deposition rate $R_B$, which is equivalent to $\alpha_B F_B$, is normally measured, rather than measuring $\alpha_B$ and $F_B$ independently. Equation (1) then becomes

\[
Q_B = F_B - \sum_{k=Ar,N} S_k F_k
\]

Now consider the dependence of an incident angle, when the boron flux $F_B$ and the ion flux coming from the same direction and parallel to each other come in contact with a curved substrate having a semicircular cross section (Fig. 1(a)). $R_B(\phi)$ and $F_i(\phi)$ depend simply on $\cos \phi$, where $\phi$ is the angle from the top of the semicircle to a certain position on the substrate surface. Indeed, there is a threshold angle close to 90° for total reflection. Sputter yield also depends on the incident angle. Thus,
\[ Q_B(\varphi) = R_B(\varphi) \cdot \sum_k k S_B(\varphi) \cdot F_k(\varphi) \]  
(Eq. 2) \[ = \{R_B(0) \cdot \sum_k k S_B(\varphi) \cdot F_k(0)\} \cos \varphi \]

Fig. 1 Schematic drawing showing the geometry of substrate and incident angle

(a) Static  (b) Turning or Waving

Fig. 2 A series of example showing dependence of atom and ion flux on incident angle to a substrate.  
(boron deposition rate : 1.3A/s, Ar ion energy: 500 eV, current density :500 \( \mu \) A/cm\(^2\).  
Sputtering yield was estimated by TRIM code.)

A series of calculated example of \( R_B(\varphi) \), \( F_{AI}(\varphi) \), \( F_{ASB}(\varphi) \), \( F_{A}(\varphi) \), and \( Q_{B}(\varphi) \) are shown in Fig. 2. At higher \( \varphi \), etching occurs due to the low arrival rate of boron and a high sputter yield, although the ion flux is low. The above description is similar to that proposed by Van Vechten et al. [16] and Hubler et al. [17].

When the substrate is turned as shown in Fig. 1(b), the general equation of average incorporation rate \( I_B \) at the point at which the angle \( \varphi \) on the semicircular surface is

\[ I_B = \frac{1}{\theta_f} \int_0^{\theta_f} Q_B(\theta + \varphi) d\theta \]  
(Eq. 3)

where \( \theta_f \) is the turned angle. The shadow effect at the back side also needs to be considered.

If the substrate is turned continuously at a constant period of rotation \( T_r \), then Eq. (3) can be given as
When the substrate is waved $\pm \theta_w$ at a constant waving period of $T_w$, then Eq. (3) becomes

$$I_B = \frac{1}{2\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} Q_B(\theta) d\theta$$

(Eq. 5)

If $\theta_w + \varphi > \pi/2$ and $\theta_w - \varphi < -\pi/2$, $Q_B(\theta + \varphi) = 0$, where $-\pi/2 < \varphi < \pi/2$, $-\pi/2 < \theta_w < \pi/2$.

A function of $d\theta/d\theta$ can be used to control the distribution of film thickness on the substrate, which itself varies as a function of $\theta$. As one of the simplified methods, consider the discrete rotation of the semicircular substrate

$$I_B(\varphi) = \frac{\sum Q_B(\theta_i + \varphi) \cdot T_i}{\sum T_i}$$

(Eq. 6)

where $\theta_i$ is the angle at which the substrate stays for a duration of $T_i$, when the angle speed is high enough that it can be ignored when compared with $T_i$.

This method is very useful since it is not easy to rotate large and heavy components. Furthermore, with regard to the crystalline structure and properties of the film, atoms and ions may have to be supplied at a certain incident angle for a certain duration in order to achieve a certain crystalline structure, without changing the angle of the substrate, since the cBN films produced by the ion beam method will have a preferential orientation that will influence the properties of the film.

Some applications require coated components to have specified film thicknesses at different positions. To achieve a uniform thickness distribution or a preferable distribution on a curved surface, the specified thickness can be determined by solving the inequalities given by

$$I_B(\varphi_j) = \frac{\sum Q_B(\theta_i + \varphi_j) \cdot T_i}{\sum T_i} > \frac{d_j}{\sum T_i}$$

(Eq. 7)

where $d_j$ is a specified thickness at position $\varphi_j$.

3. Parameter values and calculated results

3.1 Resputter yield of boron

First, the dependence of resputtering yield on an angle of incidence was estimated. It is difficult to estimate the sputtering yield during deposition with ion beam irradiation because the crystal structure and the surface composition are not the same as those inside cBN films. Friedmann et al. [7] have reported that the crystal structure of the surface was not cubic but was hexagonal. This result was derived from the measurement of the Auger boron KVV line shapes on the surface of the sample using Auger electron spectroscopy (AES). Therefore, the sputter yields of a boron nitride film with a stoichiometric composition (N/B = 1) and a density of 3.48 g/cm$^3$ (which is equivalent to cBN [18]) and those of pure boron with a density of 2.36 g/cm$^3$ were calculated using the Monte-Carlo binary encounter approximation code, TRIM [19]. The ion energy was 500 eV and the ions used were argon and
nitrogen. It was assumed that the nitrogen ions were \( \text{N}_2^+ \) since the ratio of \( \text{N}_2^+/\text{N}^+ \) with a Kaufman-type ion source at a low discharge voltage is around 10 [20], and that a \( \text{N}_2^+ \) ion having an energy of 500 eV was equivalent to two 250 eV \( \text{N}^+ \) ions [16].

Another method was used to estimate the resputter yield. Sueda et al. [12] have reported a result showing the dependence of the waving angle on the deposition rate of cBN films on a flat silicon substrate. From Eqs. (2) and (4) and the above experimental results, the dependence equation of the sputter yield of boron \( S_B \) can be reduced to

\[
\varphi S_B (\varphi + \theta) = \left\{ R_B (\varphi + \theta) - Q_B (\varphi + \theta) \right\} \frac{1}{\cos(\varphi + \theta)}
\]

(Eq. 8)

where \( \phi(\theta + \varphi) = \lambda F_B(\theta + \varphi) + \lambda F_B(\varphi + \varphi) \), \( \phi(\theta + \varphi) \) is the normalized total ion flux of argon and nitrogen ions, and \( S_B \) is the total resputtering yield of boron. The value of \( \phi(\theta + \varphi) \) is calculated from an \( \text{Ar}^+ \) flux of 500 eV, a \( \text{N}^+ \) flux of 250 eV, and the ratio of the sputtering yield of 500 eV \( \text{Ar}^+ \) to 250 eV \( \text{N}^+ \). From this calculation, the ion composition was 36% \( \text{N}_2^+ \) and 65% \( \text{Ar}^+ \), the current density was 600–1600 \( \mu\text{A/cm}^2 \), the boron deposition rate was 3.2 Å/s, and the pressure was \( 1.3 \times 10^{-2} \) Pa. In order to consider the effect of charge exchange, the gas composition and pressure at the cross section of charge exchange obtained experimentally [3] were used in order to convert the measured ion current density into flux.

Figure 3 shows the estimated sputter yields of B, calculated using the TRIM code, for a B and a BN target with 500 eV \( \text{Ar}^+ \) ions and 250 eV \( \text{N}^+ \) ions. It also shows the empirical resputtering yield deduced from Eqs. (5) and (8) and from the experimental results, which were obtained by coating while waving the flat substrate. It was found that at a lower incident angle, the empirical resputtering yield was higher than the estimated sputtering yield of B from a BN target with the density of 3.48 g/cm\(^3\) with 500 eV \( \text{Ar}^+ \) ions, while at a higher incident angle, the empirical resputtering yield was lower than the sputtering yield of B from a B target. Hereafter, this empirical resputtering yield will be mainly applied. These results confirm that special techniques are required to coat either a round or a curved substrate effectively.

![Fig. 3 Estimated sputter yields of B from a B target and a BN target with 500eV Ar\(^+\) ions and 250eV N\(^+\) ions.](image-url)
3.2 Static deposition

The dependence of the angle of incidence on the incorporation rate of B in cBN films was calculated using Eqs. (2) and the empirical resputter yield obtained in section 3.1. The results are shown in Fig. 4. As for the experimental results, the lowest threshold of ion current density was around 600 μA/cm² for static deposition at a normal incident angle. In Fig. 4, even when the lowest current density is applied, the incorporation rate of B at an incident angle $\theta \geq 42^\circ$ will be negative, which will result in etching and not deposition. With increase in ion current density, the ion/boron arrival ratio increases, while the incorporation rate of B as well as the threshold incident angle between deposition and etching decrease. Etching occurred at an ion current density of 1600 μA/cm², although the experimental data shows that it was very similar to, but not exactly, etching. The contradiction could be explained by the fact that the resputtering yield of B is not a constant value. Further discussion will be provided in section 4.

![Fig. 4 Dependence of the angle of incidence on the incorporation rate of B in cBN films](image)

3.3 Continuous turning deposition

Using the results of static deposition and the equation above, the thickness distribution in which the semi-circular substrate is rotated continuously was calculated. As expected, a uniform thickness distribution across the surface was obtained. It was found that the deposition rate was 11% of static deposition at a normal incident angle, even at the lowest current density of 600 μA/cm². If the coated area is taken into account it will about 35% of static deposition. To improve this low efficiency, appropriate masking could be effective in preventing resputtering, although this masking is not applicable for complicated-shaped components.

3.4 Continuous waving deposition

Figure 5 shows the dependence of the waving angle and the ion fluxes on the boron incorporation rate, maintaining the boron atom flux at $4.5 \times 10^{15}$ atoms/cm²/s. This result is consistent with the previous experimental result, confirming that the empirical boron resputter yield $S_B$ is suitable for proceeding with the simulation. An estimation of the dependence of the waving angle on the incorporation rate of boron at different positions of the semicircular substrate was conducted using the results of static deposition and equation. The parameters used were (i) boron deposition rate of 3.2 Å/s, (ii) ion current density of 600 μA/cm², and (iii) ion energy of 0.5 keV. The results are shown in Fig. 6. When the waving angle $\theta$ increases, the incorporation rate of boron at the top position ($\varphi = 0^\circ$) decreases. However, it increases at a high $\varphi$ position. In order to cover all the angle positions, an angle $\theta$ of at least
±75° is required. If coating is required only at positions $\varphi \geq 40°$, then an angle of ±30° may well be applied, although this results in a significant difference in thickness.

Figure 7 shows the distribution of the B incorporation rate at waving angles $\theta = 0°, ±30°, ±60°$, and ±90°. Uniform deposition distribution can be obtained with a waving angle $\theta$ of ±90°. The deposition rate, however, is 22% of the waving angle ($\theta$) of 0° and the position angle ($\varphi$) of 0°. The difference in thickness between the thickest and the thinnest film is about a factor of 2.2.

Consequently, it has been shown that the thickness distribution of cBN films on the curved substrate can be estimated using the empirical resputtering rate of boron and this simple simulation method.

**Fig. 5** Dependence of waving angle and ion flux on boron incorporation rate in cBN films

**Fig. 6** Dependence of waving angle on the incorporation rate of boron at different positions of a semicircular substrate

**Fig. 7** Distributions of the B incorporation rate on a semicircular substrate with waving angles of $\theta = 0, ±30, ±60$, and ±90°.
3.5 Discrete waving deposition

A series of experiments were conducted and their results are given in detail elsewhere [21]. One of the combinations of coating condition used was as follow: (i) boron arrival rate of 3.2 Å/s, (ii) ion energy of 0.5 keV, (iii) ion current density of 600 μA/cm², (iv) Ar + 36% N₂ gas composition fed into the ion source, and (v) pressure of 1.3 × 10⁻² Pa during deposition. A semicircular substrate was placed and automatically waved using a stepping motor driving equipment. The discrete waving angles (θ) were ±12°, ±35°, ±58°, and there were a total of 10 stopping positions per cycle. The stopping duration ratio at wave angles ±12°, ±35°, ±58° was 1:1:3. Using the above parameters and equation, the deposition rate distribution was calculated. The simulated result of the thickness distribution at the position angle ϑ of 0°, 35°, 60° was 1:1.4:0.9. The other hand, the experimental result mentioned above showed that the ratio of the cBN thickness at 0°, 35°, and 60° was 1:1.3:0.6. The results obtained by using the empirical boron resputtering yield have shown the reasonable fit within an allowable margin of error in measuring the deposited film thickness by SEM observation of the cross sections and by analyzing AES depth profiles.

4. Discussion

There were differences between the calculated sputtering yield of boron and the empirical respattering yield during deposition from the BN and the B target. It was expected that the empirical respattering yield would be higher than the calculated sputtering yield of boron nitride due to the high energy state on the surface during the cBN deposition. Also, it has been suggested that the crystalline structure on the surface of the cBN films during deposition is not cubic but is hexagonal [7], as discussed in section 3.1. In terms of the sputtering rate during Auger depth profiling, the etching rate of the cBN film was 150 A/s. However, for the hexagonal boron nitride, the etching rate was 450 A/s, compared with the value of 600 A/s for Si at the same etching conditions with Ar ion.

It should be noted that the empirical respattering yield S₉ seems to depend on the ion/atom arrival rate. Higher S₉ values were obtained at the current density of 600 μA/n², and these values were consistent with the experimental results at less than 1000 μA/cm². However, there is a slight difference in at higher ion current density. For instance, the threshold of ion current density between etching (un-coated) region and deposition (coated) region was more than 1600 μA/cm², while at 1600 μA/cm², the simulated results using the empirical S₉ show complete etching (Fig. 4).

This suggests that some modification of the S₉ is required to achieve an accurate simulation, although the region around the threshold is not imperative for practical applications. This difference implies that at higher ion/atom arriving ratios, the respattering yield is lower. This can be explained using “coverage” of fresh boron; at a high ion/atom arriving rate, the aspect is almost the same as that of etching of boron nitride by ions, and at a low ion/atom arrival rate, the aspect might be etching of boron nitride and boron atoms that are freshly arriving and have high mobility on the surface. Burat et al. [22] have shown that the sputtering yield of B during IBAD with 100% nitrogen ion bombarding decreases as a function of nitrogen ion to boron atom flux ratio γ, for γ ≥ 1, and reaches an asymptotic value of about 0.1 atoms/incident N⁺ ion at 0.5 keV. On the other hand, for γ < 1, the maximum sputtering yield was about 0.33 atoms/incident N⁺ ion. Thus, these values are different by more than a factor of 3.

In this study, since almost-stoichiometric conditions have been discussed, the difference in sputtering yield depending on the arrival rate will be less; however, it should be taken into account if simulation at higher ion/boron arriving ratios is required.

With regard to the movement of the substrate, understanding the dependence of the sputter yield on the angle of incidence is crucial in order to achieve effective coating with IBAD, especially with materials that require a high ion/atom arrival ratio to obtain a specific character.
5. Conclusion

(1) A simple model for IBAD was presented and used for predicting the thickness distribution of cBN films on curved substrates, which are static, continuously turning, continuously waving, or discretely waving.
(2) The empirical resputtering yield of boron, deduced from experimental results, and the above indicated model allows us to make the following predictions:
   (i) For static deposition, the formation of the cBN film will be achieved only at an incident angle $\theta > 40^\circ$.
   (ii) By continuous waving at a waving angle $\theta > \pm 75^\circ$, the entire semicircular substrate can be coated.
(3) The reliability of the method was confirmed by the experimental result for discrete waving deposition.

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