Mass spectrometric study of low-pressure inductively coupled plasma for chemical vapor deposition of cubic boron nitride films

To cite this article: Hangsheng Yang and Toyonobu Yoshida 2003 Sci. Technol. Adv. Mater. 4 613

View the article online for updates and enhancements.

Related content
- Influence of oxygen on the growth of cubic boron nitride thin films by plasma-enhanced chemical vapour deposition
  Yang Hang-Sheng, Nie An-Min and Qiu Fa-Min
- Synthesis of Boron Nitride Films by Microwave Plasma Chemical Vapor Deposition in Fluorine-Containing Gases
  Seiichiro Matsumoto and Wenjun Zhang
- Selective growth of boron nitride nanotubes by plasma-enhanced chemical vapor deposition at low substrate temperature
  L Guo and R N Singh

Recent citations
- Sketching functional, ubiquitous ZnO nano-sensors on paper
  N. Mohseni Kiasari et al
- Effect of magnetic field profile on the uniformity of a distributed electron cyclotron resonance plasma
  C. C. Huang et al
- Abnormal photoelectrical properties and gas sensing of mesoporous Sn0.9Ti0.1O2 film under UV light
  Zhidong Lin et al
Mass spectrometric study of low-pressure inductively coupled plasma for chemical vapor deposition of cubic boron nitride films

Hangsheng Yang, Toyonobu Yoshida*

Department of Materials Engineering, School of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan

Received 1 September 2003; accepted 21 October 2003

Abstract

Chemical species in plasma are crucial for understanding the mechanism of cubic boron nitride film vapor phase deposition and controlling the film structure. In this study, the plasma condition for cubic boron nitride deposition by low-pressure inductively coupled plasma-enhanced chemical vapor deposition using B\textsubscript{2}H\textsubscript{6}, N\textsubscript{2}, and Ar as reactant gases has been diagnosed by a quadrupole mass spectrometer with an ion energy analyzer. The ionization potentials of B\textsubscript{X}H\textsubscript{Y} (X = 1–2, Y = 0–6) decomposed from B\textsubscript{2}H\textsubscript{6} have been measured to be between 11.6 and 18.9 eV. B\textsubscript{2}H\textsubscript{6} was totally ionized to B\textsuperscript{+} together with small amounts of BH\textsuperscript{+}, BH\textsubscript{2}\textsuperscript{+} and B\textsubscript{2}H\textsubscript{Y}\textsuperscript{+} in plasma above the 2 kW input power. N\textsubscript{2} was only partially ionized, and the degree of ionization increased with increasing Ar partial pressure. Neutral species under the present plasma environment were N\textsubscript{2}, Ar and He, but N and H were not detected even by appearance mass spectrometry. Our results demonstrate that the main sources for cubic boron nitride formation are ions produced in plasma. The interaction between N\textsubscript{2} and the growth surface suppresses the cubic boron nitride formation by enhancing the tBN growth, and this surface interference can be reduced by introducing Ar into the system.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: Cubic boron nitride thin film; Quadrupole mass spectrometry; ICP-CVD

1. Introductions

Cubic boron nitride (cBN) thin films have outstanding chemical and physical properties and thus have attracted interests of a large number of researchers in the past two decades [1]. Very recently, great progress has been made in the field of cBN film vapor phase deposition. For example, thick cBN films have been prepared by direct-current jet-plasma chemical vapor deposition with the introduction of fluorine into the system [2], and hetero-epitaxial growth of cBN on special substrates has been reported [3,4]. We also found that the elimination of either an initial amorphous layer or a turbostratic BN (tBN) interfacial layer was possible with suitable pretreatments and deposition techniques even using Si as substrates [5,6]. However, the mechanism of cBN vapor phase deposition remains to be elucidated [1,7]. Further study is still required for a better understanding of the cBN nucleation and growth mechanisms. In addition, a precise diagnosis of the plasma environment is crucial.

In the present study, inductively coupled plasma-enhanced chemical vapor deposition (ICP-CVD) was applied to deposit cBN films [8,9]. A quadrupole mass spectrometer (QMS) with an ion energy analyzer (IEA) was adopted to diagnose the plasma environment. The ions and neutrals in the plasma, together with the ion energy distribution (IED), were analyzed.

2. Experimental details

The experimental apparatus was similar to that in Ref. [8], but the chamber was enlarged for large-area homogenous cBN film deposition. The 13.56 MHz RF excitation was coupled into the plasma with a three-turn coil around a water-cooled quartz tube 50 mm in diameter. The quartz tube was separated from the plasma by a 38-mm-diameter pyrolytic BN tube and a pyrolytic BN plate to minimize the contamination. N\textsubscript{2} and Ar gases (99.9999%) were fed into the reactor chamber from the top of the plasma source, while
the boron source, the commercial 10% B$_2$H$_6$ diluted in He, was introduced through a water-cooled copper probe penetrated through the plasma, and the outlet was positioned approximately 3 mm below the RF coil. The plasma was generated at approximately 1 mTorr with an input power ranging from 1 to 7 kW. Cubic BN films were deposited using a time-dependent biasing technique (TDBT) [9,10] and characterized using a Fourier transform infrared spectrometer (JASCO FT/IR-700) with transmission mode and an analysis area of 200 × 200 μm$^2$ at normal incidence.

The differentially pumped QMS with an IEA (Hiden Analytical Limited EQP 3.1 spectrometer) was mounted on the substrate holder, and connected to an ion extractor with a 100 μm aperture. The aperture was positioned approximately 50 mm below the RF coil. In the neutral species measurement, the impact electron energy was set at 70 eV with an emission current of 100 mA. In appearance mass spectrometry, the electron energy was scanned from 10 to 40 eV with an energy step of 0.1 eV and an emission current of 100 mA. In the IED analysis, the substrate and its holder were removed, and no bias was applied.

### 3. Results and discussions

Table 1 lists the measured ionization potentials of the B$_X$H$_Y$ ($X = 1–2$, $Y = 0–6$) species decomposed from the B$_2$H$_6$ + He + N$_2$ + Ar mixture gas system without plasma. The energy scale was calibrated by measuring the Ar (15.8 eV) and He (24.5 eV) ionization thresholds. The interference of the B isotope can be eliminated according to Ref. [11]. The values measured in the present study are in good agreement with those in the literature [11,12].

**Table 1** Appearance potential data of B$_X$H$_Y$ ($X = 1–2$, $Y = 0–6$) species decomposed from a B$_2$H$_6$/N$_2$/Ar mixture gas system without plasma

| Species | This work (eV) | Refs. [11,12] | Source gas |
|---------|---------------|---------------|------------|
| B       | 18.9          | 18.4          | Ar + He + B$_2$H$_6$ |
| BH      | 17.9          | 16.4          | Ar + He + B$_2$H$_6$ |
| BH$_2$  | 16.0          | 15.5          | Ar + He + B$_2$H$_6$ |
| BH$_3$  | 15.1          | 14.9          | Ar + He + B$_2$H$_6$ |
| B$_2$H$_2$ | 14.2      | 14.0          | Ar + He + B$_2$H$_6$ |
| B$_2$H$_4$ | 13.2      | 14.2          | Ar + He + B$_2$H$_6$ |
| B$_2$H$_6$ | 12.5      | 12.4          | Ar + He + B$_2$H$_6$ |
| B$_2$H$_8$ | 12.0      | 11.9          | Ar + He + B$_2$H$_6$ |
| B$_2$H$_{10}$ | 11.6    | –             | Ar + He + B$_2$H$_6$ |

**Fig. 1.** Neutral mass spectrum under the plasma condition for film deposition. Gas flow rates were 19 sccm Ar, 0.7 sccm N$_2$ and 7 sccm B$_2$H$_6$ diluted with He.

**Fig. 2.** Ion species under the same plasma conditions as those in Fig. 1.

are considered to be the main neutrals under this plasma environment for film deposition. Note that the signal of He is also weak in Fig. 1 due to its small ionization cross-section. Fig. 2 shows the contents of ions under the same condition as that in Fig. 1. Besides the ions of Ar$^+$, N$^+$, N$_2^+$ and He$^+$, BH$_X^+$ ($X = 0–2$), particularly B$^+$ ions that are the main products of diborane ionization, with small amounts of B$_2$H$_Y^+$ ($Y = 1–5$) are measured. Moreover, in contrast to the very low contents of neutral H and H$_2$, high contents of H$^+$ and H$_2^+$ were detected. Accordingly, the boron source gas, B$_2$H$_6$, is completely ionized, but not decomposed to neutrals, under the plasma conditions above 2 kW input power.

**Fig. 3** shows the cBN growth rate, ion contents and the relative ion fluxes normalized by their concentrations plotted as a function of [N$_2$/(N$_2$ + Ar)], respectively. **Fig. 3a** can be divided into three parts: films with a pure cubic phase upper layer are prepared in region B, merely tBN films or tBN/cBN mixture films are deposited in region C, while region A is the sputtering-effects-dominated region, and almost no film can be deposited on the substrate when the B$_2$H$_6$ and N$_2$ concentrations are below 2%. **Fig. 3b** illustrates that the content of ions corresponding to nitrogen (N$_2^+$ and N$^+$) and total ion content (Ar$^+$ + N$^+$ + N$_2^+$) increase slightly with increasing N$_2$ concentration, while that of Ar$^+$ decreases slightly. When the N$_2$ concentration
increases from 2 to 18%, the content of ions corresponding to nitrogen ($N_2^+$) increases only from approximately $3.0 \times 10^7$ to $7.5 \times 10^7$ (in arbitrary units), indicating a decrease in the degree of $N_2$ ionization. Moreover, the $N^+$ content is revealed to approximately equal that of $N_2^+$ in $N_2^+$Ar plasma and to be even higher than that of $N_2^+$ at lower $N_2$ concentrations, while the $N^+$ content is found to be much lower than that of $N_2^+$ in pure $N_2$ plasma. Therefore, $N_2$ in plasma is only partially ionized, and the introduction of Ar into the $N_2$ plasma enhances the degree of $N_2$ ionization, and in particular $N^+$ content, in agreement with Wang and Olthoff’s measurements [13]. Since the exact degree of ionization is difficult to measure, we used the relative ion flux normalized by its concentration ($F_R = \text{ion content/concentration}$) to evaluate the degree of ionization. As is shown in Fig. 3c, $F_{R,N^+}$ and $F_{R,N_2^+}$ decrease sharply with a slight increase in the $N_2$ concentration, particularly at lower concentrations, while $F_{R,Ar^+}$ remains almost constant.

Films with a pure cBN upper layer can only be prepared under the environment of high $F_{R,N_2^+}$ and $F_{R,N_2^+}$, which suggests that the degree of $N_2$ ionization, but not the degree of Ar ionization, controls the cBN growth. From Fig. 3, it is also evident that the cBN growth rate increases with increasing content of ions corresponding to nitrogen ($N_2^+ + N^+$) in region B. This finding suggests that, in the present ICP-CVD process, $N^+$ or $N_2^+$ ions are the main nitrogen source for cBN formation. However, the cBN growth rate then decreases even though the $N^+ + N_2^+$ content continues to increase as the $N_2$ concentration exceeds approximately 8%, under the environment of low $F_{R,N^+}$ and $F_{R,N_2^+}$. Because the neutrals under these plasma conditions are $N_2$, He and Ar, $N_2$ is considered to be the main neutral to interact with the growth surface, and this interaction suppresses the cBN formation.

Fig. 4 shows the $sp^2$-bonded BN and cBN growth rate plotted as a function of $N_2/(N_2 + Ar)$. On the right-hand side where the $N_2$ concentration was higher than 10%, the $sp^2$-bonded BN growth rate increased quickly with increasing $N_2$ concentration. At the same time, the cBN growth rate decreased, and the upper layer of the prepared films became merely tBN films or tBN/cBN mixture films [9,10]. Thus, the increase in the $N_2$ concentration in plasma enhanced the tBN growth, leading to the suppression of cBN growth.

Because of a low degree of $N_2$ ionization under the present plasma conditions, in the time span between two ion bombardments, the interaction between neutral $N_2$ and the growth surface cannot be neglected. In addition, it was found that the source species for BN growth are $N^+$, $N_2^+$, $BH_3^+$, $B_2H_4^+$ ions and $N_2$. For the case of a high Ar concentration, the neutral is mainly Ar, therefore the interaction between $N_2$ (including excited $N_2^*$ by plasma) and the growth surface is suppressed, and accordingly, films with a pure cBN upper layer can be prepared. With increasing $N_2$ concentration, the interaction between $N_2^*$...
and the growth surface becomes more and more important. Note that the existence of an ion energy window [8,9] for cBN growth in the present process indicates that below a certain ion energy threshold, only tBN can be prepared. Accordingly, the tBN growth rate increases with increasing N2 concentration, leading to the decrease in the cBN growth rate. In the case of the mass-separated ion-beam deposition process, only 14N+ and 11B+ have been used, without the assistance of Ar+ bombardment, but cBN films with more than 85% cubic phase have been prepared [14]. This again indicates that the interaction between the N2 and the growth surface is the main reason for suppressing the cBN formation in the present process. Introduction of Ar into the plasma successfully reduces the interaction between the N2 and the growth surface, and at the same time, the degree of N2 ionization is also increased, thus enhancing the cBN growth.

4. Conclusions

In summary, the QMS-IEA analysis of the ICP-CVD system revealed that the entire B source existed as ions, while N2 was only partly ionized. Chemical species under the present plasma conditions were revealed to be N+, N2+, Ar+, H+, H2+, He+, BH+, B2H+, N2, Ar and He. The main sources for cubic BN formation are ions produced by plasma in the ICP-CVD process. The interaction between N2 and the growth surface resulted in tBN growth thus leading to the suppression of cBN growth, and this surface interference can be reduced by the introduction of Ar into the system.

Acknowledgements

The present research was financially supported by a Grant-in-Aid for Scientific Research (A) (Grant No. 13355028) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. H.S. Yang acknowledges the support of the Japan Society for the Promotion of Science (JSPS) during this work (ID No: P03055).

References

[1] T. Yoshida, Diamond Rel. Mater. 5 (1996) 501.
[2] S. Matsumoto, Z. Wenjun, Jpn. J. Appl. Phys. 39 (2000) L442.
[3] H. Feldermann, C. Ronning, H. Hofsass, J. Appl. Phys. 90 (2001) 3248.
[4] Z.W. Zhang, H.-G. Boyen, N. Deyneka, P. Ziemann, F. Banhart, M. Schreck, Nat. Mater. 2 (2003) 312.
[5] C. Iwamoto, H.S. Yang, T. Yoshida, Diamond Rel. Mater. 11 (2002) 1854.
[6] H.S. Yang, C. Iwamoto, T. Yoshida, J. Appl. Phys. 94 (2003) 1248.
[7] P.B. Mirkarimi, K.F. McCarty, D.L. Medlin, Mater. Sci. Engng R21 (1997) 47.
[8] T. Ichiki, T. Moosoe, T. Yoshida, J. Appl. Phys. 75 (1994) 1330.
[9] H.S. Yang, C. Iwamoto, T. Yoshida, Thin Solid Films 407 (2002) 67.
[10] H.S. Yang, C. Iwamoto, T. Yoshida, J. Appl. Phys. 91 (2002) 6695.
[11] J.H. Wilson, H.A. McGee Jr., J. Chem. Phys. 46 (1967) 1444.
[12] W.S. Koski, J.J. Kaufman, C.F. Pachucki, F.J. Shipko, J. Am. Chem. Soc. 80 (1958) 3202.
[13] Y. Wang, J. Olthoff, J. Appl. Phys. 85 (1999) 6358.
[14] H. Hofass, C. Ronning, U. Griesmeier, M. Gross, S. Reinke, M. Kuhr, Appl. Phys. Lett. 67 (1995) 46.