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DEPOSITION OF c-BN FILMS BY PULSED DC BIASING IN MAGNETICALLY ENHANCED ARE METHOD

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Abstract

BN films were grown on silicon (100) substrate by magnetically enhanced activated reactive evaporation (ME-ARE) with pulsed DC power instead of r.f. for substrate biasing. The deposited films were analyzed using Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM). FTIR results show that the intensity of absorption band of sp^2 bond of BN decreased and that of sp^3 bond of c-BN increased with increasing pulsed DC bias voltage applied to substrate. The initially grown layer at the interface was observed by TEM and considered to be of sp^2-bonded BN. The cross-sectional and planar TEM micrographs show that the upper layer on the initial layer was the single phase c-BN. It is concluded that cubic boron nitride films could be synthesized by ME-ARE process with pulsed DC biasing.

Key words : *cubic boron nitride film, ME-ARE, pulsed DC*

1. INTRODUCTION

Cubic boron nitride (c-BN) has a promising potential as coatings for cutting tools, optics, and electronic devices etc. because of its unique properties comparable to those of diamond. Successful synthesis of BN films with a high content (> 85%) of the cubic phase has been reported by many different deposition processes including an ion-assisted electron-beam evaporation referred to as 'ion plating'[1)-3)]. For the synthesis of BN films with a high content of c-BN, the energetic-particle (mainly ion) bombardment during film growth is necessary. In general, r.f. power has been employed to accelerate ions to the growing film in ion-assisted electron-beam evaporation[3),4)]. In this study, c-BN films were deposited by magnetically enhanced activated reactive evaporation technique. Pulsed DC power instead of r.f. for substrate biasing was used.

2. EXPERIMENTAL

The synthesis of BN films was performed through activated reactive evaporation of boron vapor and nitrogen ion in ME-ARE system illustrated in Fig. 1. 99.9% pure metal boron was used as the evaporation source material. The plasma discharge of argon and nitrogen gases introduced into the reaction chamber was generated between the hot filament cathode and the auxiliary anode with positive potential. Parallel magnetic field induced by a pair of magnets intensified the generated plasma.

The substrates used in this study were (100) single crystal silicon. The substrates were cleaned by dipping in 10% HF for five minute. After evacuating the chamber down to a base pressure of 5×10^{-6}torr, a processing pressure of 4×10^{-4}torr was maintained during the deposition. The substrate was heated by the graphite heater. The substrate temperature was measured with a thermocouple placed on the backside of the substrate holder. An additional pulsed DC power for biasing was applied to the substrate to grow cubic BN films. The deposition of BN films was performed in the ranges of the parameters shown in Table 1. Taguchi method was employed to evaluate the degree of contribution of the pulsed DC power and other parameters to the formation of c-BN.

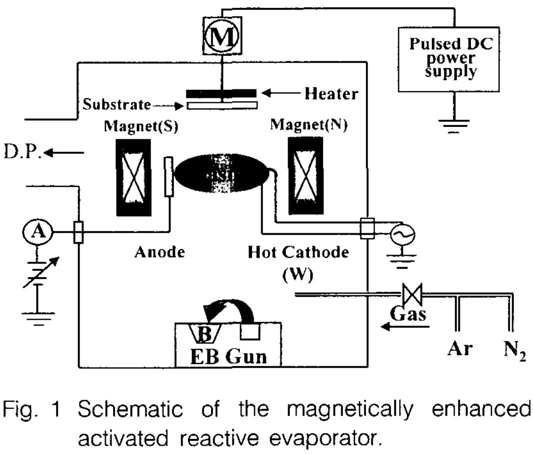


Fig. 1 Schematic of the magnetically enhanced activated reactive evaporator.

Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM) were used to obtain a clear evidence for the phase of the BN films.

3. RESULTS AND DISCUSSION

Fig. 2 is the FTIR absorption spectra for the films deposited at various pulsed DC substrate bias voltages from 100 to 150V. Duty and frequency of the pulsed DC power were maintained at 50% and 1kHz, respectively. The plasma discharge current, the gas flow ratio of argon to nitrogen (R[Ar/N_2]), and the substrate temperature was 10A, 3, and 500℃, respectively.

The dominant primary and secondary absorption bands near 1400cm^{-1} and 800cm^{-1} in the upper two spectra are correspondent to sp^2 bond of BN (mainly h-BN). As the pulsed DC substrate bias increased, the characteristic absorption bands of sp^2 bond of BN disappeared

Table 1. Experimental conditions for the deposition of BN films.

Ar/N_2 gas flow ratio	1~10
Substrate Bias Voltage (-V)	50~200
Duty (%)	20~80
Frequency (kHz)	1~40
Plasma discharge current (A)	5~15
Substrate temperature (℃)	300~900
Electron beam power (kW)	1.8~2.0
Magnetic field strength (G)	45~55

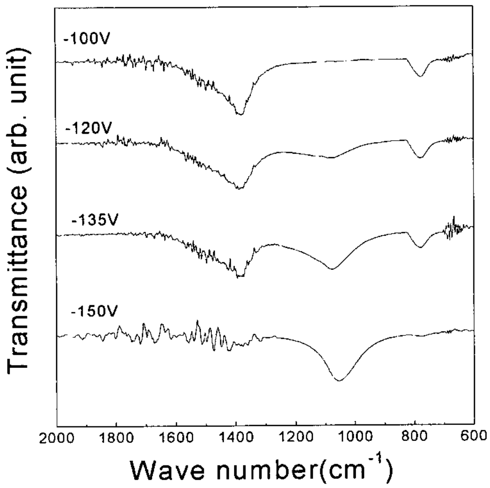


Fig. 2 FTIR spectra of BN films deposited at various pulsed DC bias voltages.

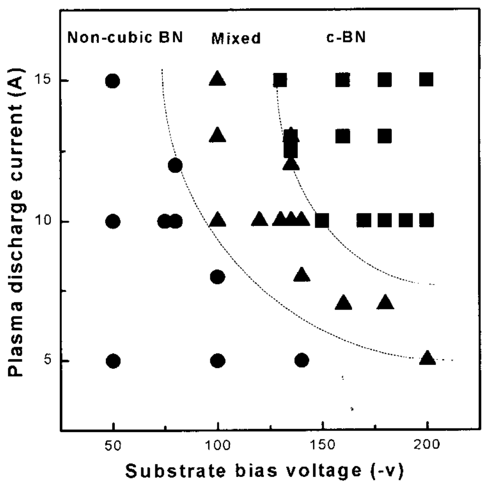


Fig. 3 Processing map of plasma discharge current and pulsed DC substrate bias voltage for BN film deposition.

gradually and a strong absorption band near 1080cm^{-1} corresponding to c-BN sp^3 bond appeared at the pulsed DC substrate bias of 150V. The effects of pulsed DC substrate bias voltage and plasma discharge current on the grown BN films were summarized in Fig. 3. In case of the plasma discharge current lower than 5A, only h-BN was grown although the pulsed DC substrate bias was as high as 150V. The critical values of the plasma discharge current and the pulsed DC substrate bias voltage to get BN films with a high content (> 85%) of the cubic phase were 10A and 150V, respectively. Above the value of 15A, 200V, BN films were resputtered by excessive ion bombardment during the deposition. This growth behavior was the same as that in the BN growth using r.f. substrate bias.

To investigate the effects of processing parameters on the formation of c-BN, the eight parameters were selected and each parameter was in three levels. A set of experiments to apply Taguchi method was conducted according to the L18($2^1 \times 3^7$) orthogonal array table composed of the eight parameters and their three levels. Analysis of variance(ANOVA) of c-BN content of resultant BN films was illustrated in Fig. 4. It shows the degree of contribution of the pulsed DC power and other parameters to the formation of c-BN. Degree of contribution of pulsed DC substrate bias voltage(Vb), duty, and frequency obtained from ANOVA were 26.4%, 28.3%, and 15.0%, respectively. These values were two or six times greater than that of other parameters. These results indicate that the three parameters were the key factors for the formation of the cubic phase.

The cross-sectional TEM micrograph and selected area diffraction pattern(SADP) of c-BN films deposited on(100) Si substrate under an optimum condition is shown in Fig. 5(a). As shown in the micrograph, the film, 0.18㎛ thick, consisted of two distinct layers. The initially

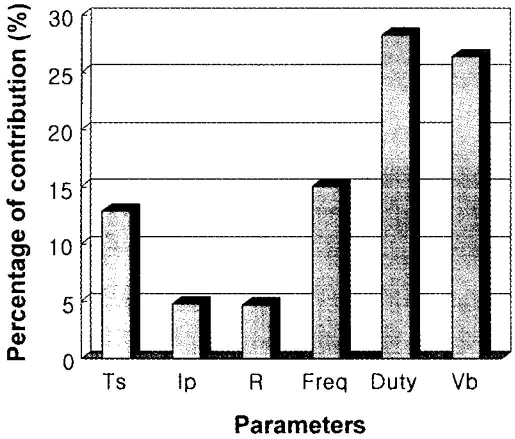
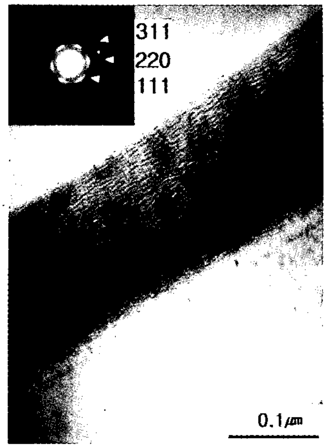
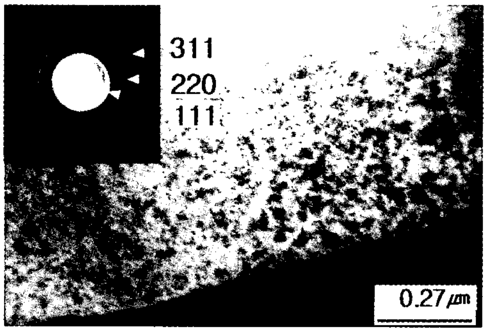


Fig. 4 Degree of contribution of the pulsed DC power and other parameters to the formation of c-BN.



(a) cross-sectional view



(b) planar view

Fig. 5 TEM micrograph and diffraction for c-BN film.

grown layer at the interface, ~0.02μm thick, is columnar-structured and considered of sp2-bonded BN as previously reported by other researchers[5),6)]. The upper layer appeared quite different from the initial layer in microstructure, and the SADP was of cubic phase of BN. Fig. 5 (b) shows a planar TEM micrograph of the same sample prepared by back-thinnig method. In the SADP of the upper layer, the interplanar spacing of (111), (200), and (311) planes was in good agreement with that of bulk zinc-blende BN with a lattice constant of a=3.6158Å. The diffraction rings also indicates that the c-BN film consisted of the very fine polycrystallites. From these TEM results, it is concluded that the upper layer was of the single phase c-BN.

5. CONCLUSION

Single phase c-BN films were successfully synthesized on Si(100) substrate by pulsed DC biasing in magnetically enhanced activated reactive evaporation method. Deposition behavior of BN films was the same as that in the BN growth using r.f. substrate bias. It was found that pulsed DC substrate bias voltage, duty, and frequency of the pulsed DC power were the most important deposition parameters for the formation of the cubic phase.

REFERENCES

1. M. Okamoto, Y. Yokoyama, and Y. Osaka,

Jpn. J. Appl. Phys. 29. P. 930 (1990)
2. D. J. Kester, K. S. Ailey, D. J. Lichtenwalner, and R. F. Davis, J. Vac. Sci. Technol. A 12, 3074 (1994)
3. S. Watanabe and M. Murakawa, Surf. Coat. Technol., 43/44, 137-144 (1990)
4. T. Ikeda, Y. Kawate, and Y. Hirai. J. Vac. Sci. Technol. A 8 3168 (1990)
5. D. L. Medlin, T. A. Friedmann, P. B. Mirkarimi, P. Rez, M. J. Mills, and K. F. McCarty. J. Appl. Phys., 76 295-303 (1994)
6. D. J. Kester, K. S. Ailey, and R. F. Davis. J. Mater. Res., 8(6) 1213 (1993)