논 문
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EAHFCVD법에 의한 c-BN 박막형성기구와 계면층의 특성에 관하여

Characteristics on Boundary Layer and Formation Mechanism of c-BN Thin Films During Electron Assisted Hot Filament CVD Process

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(Yong Choi · Jean I. Choe)

Abstract - c-BN films were deposited on SKH-51 steels by electron assisted hot filament CVD method and microstructure development was studied processing parameters such as bias voltage, temperature, etching and phase transformation at boundary layer between BN compound and steel to develop a high performance wear resistance tools. A negative bias voltage higher than 200V at substrate temperature of 800℃ and gas pressure of 20 torr in B2H6-NH3-H2 gas system was one of optimum conditions to produce c-BN films on the SKH-51 steels. Thin layer of hexagonal boron nitride phase was observed at the interface between c-BN layer and substrate.

Key Words : Cubic boron nitride phase, Electron assisted hot filament CVD, Bias voltage

1. Introduction

BN compound represents the existence of variety phase such as c-BN, h-BN, w-BN, r-BN and t-BN due to bonding formation[1-5]. c-BN related to sp3 hybridization bonding among these materials has much excellent characteristic properties such as low density, extreme hardness, large thermal conductivity, wide band gap of 6.4eV, high breakdown voltage of 80x10^5V/cm and high thermal stability[6-7]. Thus, c-BN should be possible to apply to ferrous metals for wear resistance in contrast to diamond, which it was transformed to graphite when coating diamond on ferrous metal by gas phase method[8]. Thin BN film can be prepared by various deposition techniques like rf-sputtering, ion-beam assisted deposition, rf-plasmaCVD, electron cyclotron resonance plasma CVD and microwave plasma enhanced CVD[9]. Thermal filament CVD process has a problem of slow deposition rate but it has characteristic properties of wide area with homogeneous deposition layer [10]. Although textured and epitaxial growth on different substrate by CVD technique have been reported[11], it is hard to fabricate high cubic phase content BN films with the absence of further evidence because of relatively poor repeatability and rigorous craft.

Hence, in this study, the effects of fabrication parameters like composition of inlet gas, flow rate, pressure, substrate temperature, bias voltage were systematically studied to establish an optimum condition. Emphasis is on the microstructure development of BN at the interface between matrix and substrate.

2. Experimental procedure

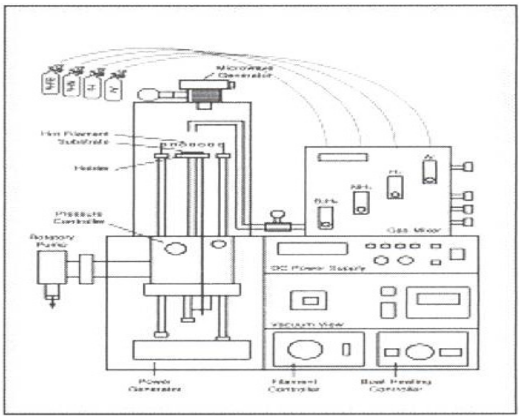

Fig. 1 Schematic diagram of microwave plasma assisted hot filament CVD system

The schematic diagram of EACVD is shown in Fig. 1. The substrate was heated to 600-800℃ by two electrodes which connected to an AC power and negative bias voltage was connected to filament. 2.45 GHz microwave used was generated plasma by magnetron and

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transmitted with the circle waveguide. Microwave plasma deposition reactor was fabricated to cavity with magnetron which it was made of Al box of 270*160*350mm size. The chamber was evacuated to 20-80 Torr and then refilled with B_2H_6, NH_3, H_2 which was diluted to 10% by Ar.

Table 1 shows general composition of substrate

	C	Si	Mn	Cr	W	Mo	V
SKH51	0.8-0.9	<0.4	<0.4	3.8-4.5	5.5-6.7	4.5-5.5	1.6-2.2

3. Result and Discursion

The crystallization and surface morphology of c-BN film is depend on deposition technique and deposition condition such as pressure, flow rate, substrate composition and temperature[12]. Fig. 2 shows surface microstructure with temperature that obtained to experimental conditions as Table 4, which was total flow rate of 2000 Sccm. It was shown well defined facets of BN at substrate temperature of 800℃

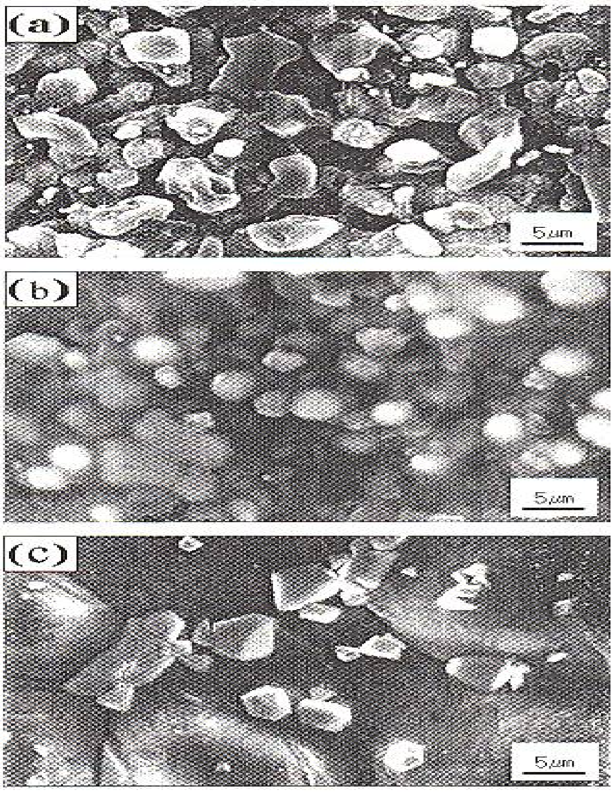


Fig. 2 SEM micrographs ; (a) 600℃ ; (b) 700℃ ; (c) 800℃

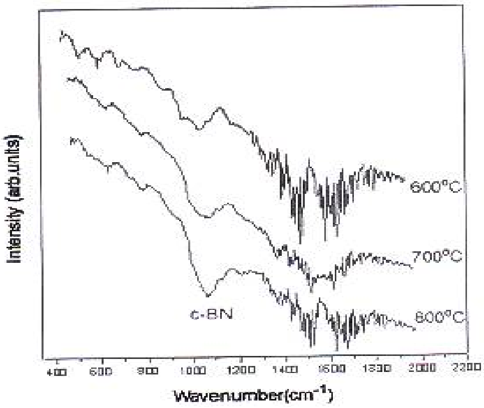


Fig. 3 FT-IR spectra of BN films deposited at different temperature

Fig. 3 is FT-IR spectra of BN films deposited at different temperature with a negative bias of 300V. No cubic phase was detected in the boron nitride films at low substrate temperature (700℃). It is due to the formation of hexagonal phase as revealed by the h-BN TO frequency at 800 cm^{-1} because sp2 bonded BN is usually disordered[13]. The growth mechanism may essentially be governed by etching of hexagonal phase and the depositon of cubic phase due to ion with high level energy and ion bombardment[14]. That is, inleted ions with much energy of inside materials provide energy to around atoms. Then compressive stress occurred due to active electronic motion of these atoms inside of films[15] . Setiz reported[16] that ion bombardment with much energy induced phase transformation to c-BN from h-BN, since displacement of atoms prompts the formation of c-BN. Fig. 4 is FT-IR spectroscopy of BN films with different thickness at the etched region.

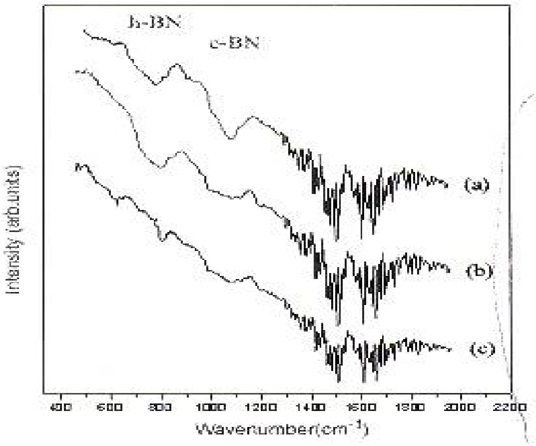


Fig. 4 FT-IR spectroscopy of BN films measured at different Etching time (a) 50min; (b) 65min; (c) 90min.

FT-IR absorption spectra of the remaining BN films at the edge region shows a mixture of c-BN and h-BN phase when the film was etched for 50 min. But in case of etching for 65 min, FT-IR exhibits a mostly h-BN phase remaining in BN films at the etched region. As well as self-bias increases, the sputter etching of high energy ions decrease the film thickness. It means the peaks responding to c-BN phase became very weak due to long time etching.

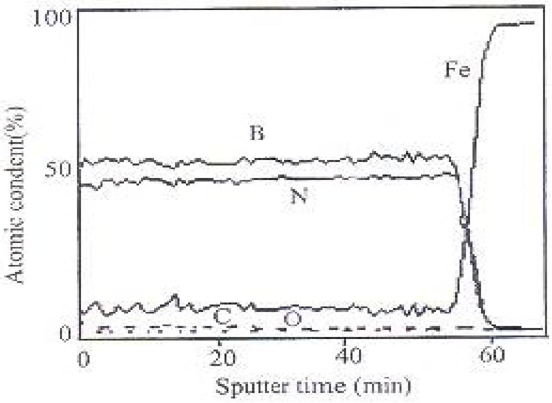


Fig. 5 Auger depth profiles of c-BN film

The Auger spectrum of the cubic boron nitride films deposited at temperature of 800℃ with a negative bias of 300V is shown in Fig. 5 The film is consist mainly of boron and nitrogen. The ratio of B and N in film is very close to 1:1. The impurities of carbon and oxygen are due to capture during the film growth and it's environmental interaction after deposition. Fig. 6 shows cross sectional SEM micrograph at interface of BN films deposited on SKH51 steel. h-BN phase of thin bright layer is observed at the interface between c-BN phase and SKH51 steel.

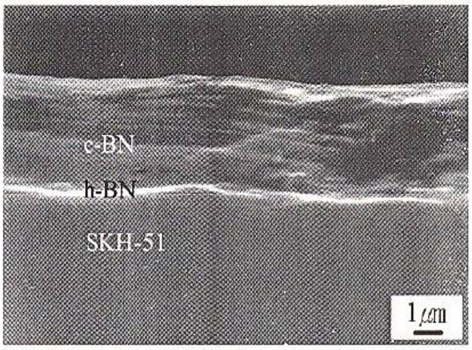


Fig. 6 Cross sectional SEM micrograph of films deposited on SKH 51 substrate.

It was confirmed by FT-IR spectrum. The presence of interfacial h-BN phase is probably attributed to lower compressive stress during initial deposition than critical value which cause transformation of c-BN from h-BN phase. That is, h-BN of sp2 bonding during initial deposition transformed to c-BN of sp3 bonding state due to compressive stress by ion bombardment with high energy[17].

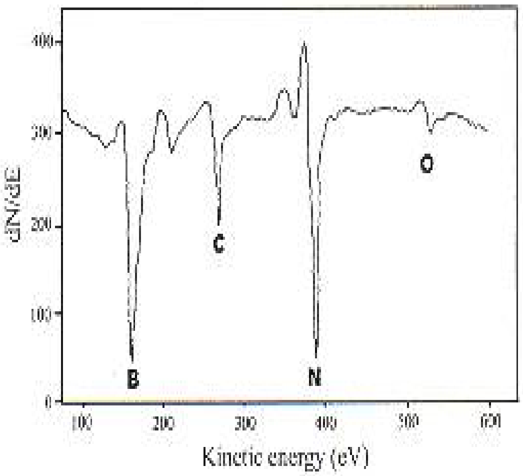
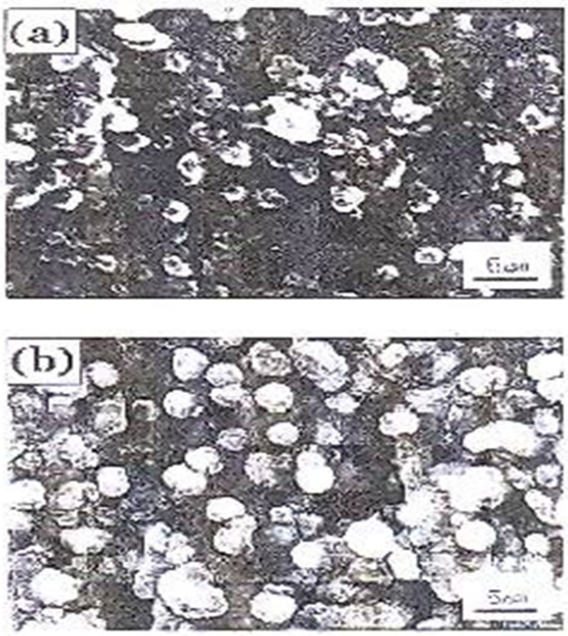


Fig. 7 Auger spectrum of c-BN film

Fig. 7 is Auger depth concentration profiles of c-BN Films. No other contamination with the exception of carbon and oxygen were detected in films. Moreover, carbon and oxygen shows constant line. Therefore, nearly the films of stoichiometric composition with high purity and excellent crystal facet have been prepared in this experiment. Fig. 8 is SEM micrographs at various bias voltage. It shows that facet of BN films is not well developed without applied bias. Well defined facets of BN were observed in condition of 300 voltage.



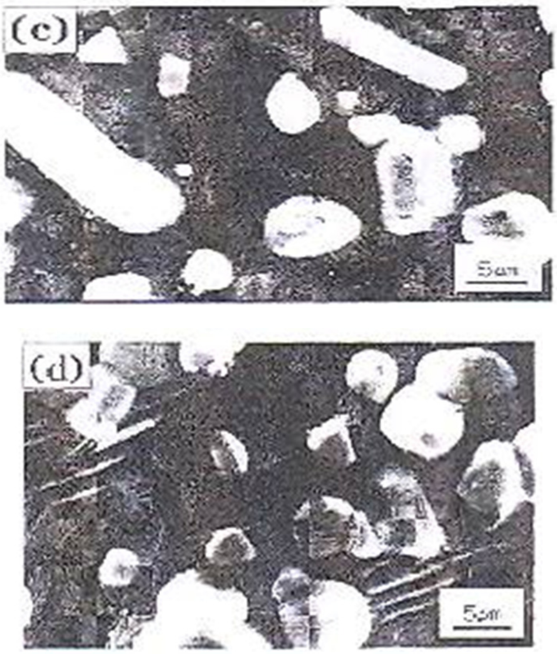


Fig. 8 SEM micrographs ; (a) no bias; (b) −100V; (c) −200V; (d) −300V

Charged negative voltage to filament and positive voltage to substrate is not only prevent the carburization of filament but also prompt the nucleation and growth. Since, BN radicals of negative ion attracts to substrate charged positive voltage[18]. Moreover, it was expected to increase concentration of BN radical due to acceleration of reaction and decomposition of NH3, B2H6 on substrate. In order to further confirmed above conclusion, FTIR absorption spectroscopy was used to determine BN films with various bias voltage. As shown in Fig. 9, FT-IR spectra near 1080 cm^{-1} is assigned to the TO mode of cubic BN at substrate temperature of 800℃ with a negative bias of 300V. It implies that there is no strong damage even with high energy by continuous bombardment of ions on BN surface during growth[19].

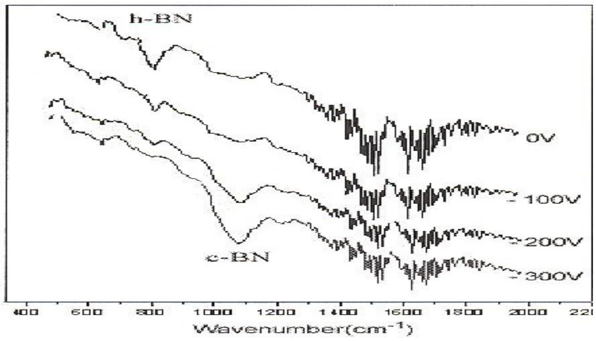


Fig. 9 FTIR spectra of BN films with various Bias voltage at substrate temperature of 800℃

3. Conclusion

Characterization of interface layer of c-BN films formed by electron assistant hot filament CVD were carried out at bias voltage and temperature. Excellent c-BN phase was represented at total flow rate of 2000Sccm, pressure of 20Torr, negative bias of 300V and substrate of 800℃ in B2H6-NH3-H2 gas system. It shows fast film growth with increasing bias voltage until negative bias voltage of 300V. Concentration of BN radicals on substrate increases due to accelerating decomposition of gas species and synthesis of BN compound by thermal electron generated on filament. Thin layer of h-BN exists at the interface between c-BN and substrate . It results from the phase transformation of h-BN to c-BN by high energy ions and ion bombardment.

감사의 글

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