

Characterization of interface of c-BN film deposited on silicon(100) substrate

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Abstract

The interfacial microstructure of cubic boron nitride (c-BN) film deposited on single silicon substrate using magnetically enhanced active reaction evaporation (ME-ARE) has been investigated through thinning methods, in which X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) absorption spectroscopy were used for compositional and microstructure analysis. c-BN film was etched at size $4 \times 4 \text{ mm}^2$ by argon ion in XPS equipment to obtain depth concentration profile of the BN film and B1s XPS spectra at different etching depth. FTIR was alternately used to determine the microstructure of the BN film at different etching depth. The results show that a thin layer of hexagonal boron nitride (h-BN) phase exists at the interface between c-BN layer and substrate. In addition, transmission electron microscopy and selected area electron diffraction further confirm above the conclusion. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Boron nitride

1. Introduction

Owing to its excellent physical and chemical properties such as extreme high hardness, high wear resistance, high chemical and thermal stability, c-BN has a promising application in coating for cutting tools, optics and electronic devices etc. Recently several PVD and CVD techniques have been developed to synthesize c-BN films under low-pressures [1–6]. It has been reported that ion bombardment with low energy to growing film is very important for successful growth of c-BN film [7]. However, the details of c-BN film growth mechanism has not been fully understood. The commonly used methods to study growth of c-BN film are Fourier transform infrared absorption spectroscopy (FTIR) and HRTEM [8,9]. In this work, X-ray photoelectron spectroscopy (XPS), combined with FTIR and transmission electron microscopy (TEM) was used to investigate the growth of c-BN film deposited on silicon substrate by magnetically enhanced active reaction evaporation (ME-ARE). For XPS analysis of BN film, π bond shake-up satellite of B1s XPS appears only in h-BN phase, but not in c-BN phase [10]. In addition, c-BN film is etched at size $4 \times 4 \text{ mm}^2$ by argon ions in XPS equipment without changing

microstructure of BN so that FTIR absorption spectroscopy can be used to confirm the microstructure of BN film with various thicknesses at the etched region, which, in fact, responds to different growing stages. Conclusive information about interfacial microstructure between c-BN layer and substrate is obtained by a combination of XPS, FTIR and TEM characterization.

2. Experiment

c-BN films for investigation were prepared using ME-ARE method. In this method, c-BN film was deposited on Si(100) through evaporation of pure boron by electron beam, followed by reaction of evaporated boron with high-density nitrogen ions supplied to substrate. A parallel magnetic field was used to enhance plasma discharge between a hot cathode and anode. A r.f. bias was applied to substrate in order to cause the ions to bombard the growing film and promote the formation of c-BN phase. The optimum conditions for deposition of c-BN and h-BN film were summarized in Table 1.

As deposited c-BN film was characterized by XPS and FTIR and TEM. The film was etched at size $4 \times 4 \text{ mm}^2$ by 3 KeV argon ions to obtain depth concentration profile of the film. The B1s core level XPS spectra responding to surface of remained BN film with various thicknesses at the etched

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Table 1
The optimum conditions for deposition of c-BN and h-BN film

Deposition conditions	c-BN	h-BN
Working pressure (Pa)	$4-6 \times 10^{-2}$	$4-6 \times 10^{-2}$
Substrate r.f. bias (V)	-200	0
Discharge current (A)	15	15
Ar/N ₂ flow ratio	5	5
EB gun power (kW)	1.4	1.4
Substrate temperature (°C)	400	400
Deposition time (min)	20	20

region were measured, followed by microstructural identification of BN film with various thicknesses at the etched region using FTIR absorption spectroscopy.

3. Results and discussion

Fig. 1 shows the FTIR absorption spectroscopy of c-BN film deposited under optimum conditions. It has a strong characteristic peak of c-BN band near 1080 cm^{-1} with the weak B-N stretching peak and B-N-B bending peak at 1380 and 780 cm^{-1} , respectively, which indicates that the BN film is mostly c-BN phase with a small amount of h-BN phase. Fig. 2 shows the depth concentration profile of above the c-BN film. A nearly stoichiometric BN film was obtained. The arrows with numbers indicate the positions at which the B1s XPS spectrum and FTIR absorption spectroscopy responding to various BN film thickness at etched region were measured, as shown in Figs. 3 and 4, respectively.

Fig. 3 shows the variation of B1s XPS spectra measured at 45° take off angle with etching time. The binding energies 190.7 eV respond to metallic boron in BN, which are in agreement with in literature value [7]. When the film was etched for 120 and 140 min, respectively, a broad weak peak appeared at about 7.5 eV higher binding energy than core level peak (190.7 eV) in B1s XPS spectra (Fig. 3c,d), but not

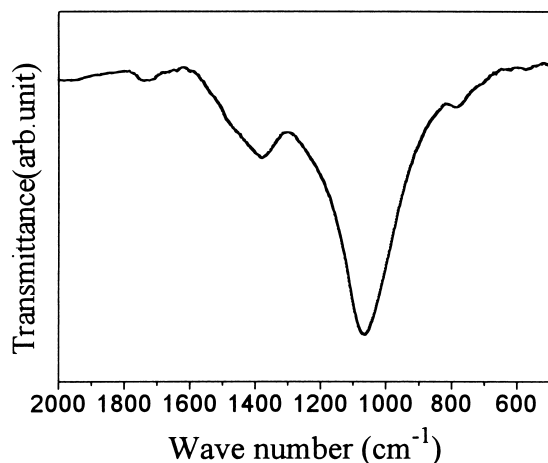


Fig. 1. FTIR spectroscopy of c-BN film deposited at a r.f. bias of -200 V .

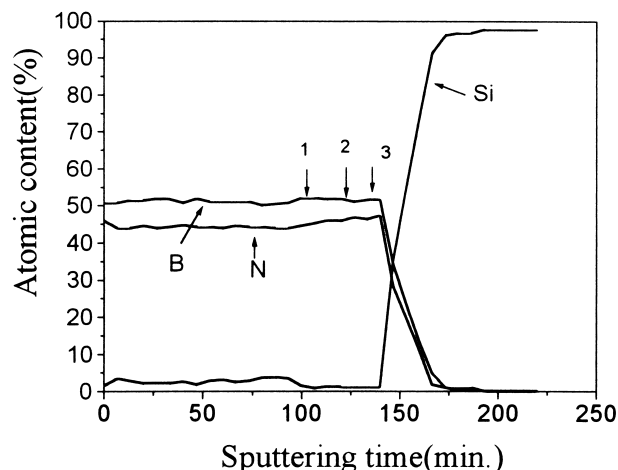


Fig. 2. XPS depth concentration profile of c-BN film deposited at a r.f. bias of -200 V .

in B1s XPS spectrum measured at surface (Fig. 3a) of the film in which only c-BN phase exists. It has been previously reported that bond shake up satellite of B1s XPS is associated with the $\pi-\pi^*$ transition in sp^2 -bonded h-BN phase. Thus it is speculated that h-BN phase exists in BN film near the substrate. Fig. 5 shows the core level B1s XPS spectra of pure h-BN films taken at the surface (Fig. 5a) and after etching for 20 min (Fig. 5b), respectively. They exhibit almost the same spectra with bond shake up satellites indicating ion etching did not change the crystalline structure of BN film, which supports the result of Fig. 3.

In order to further confirm above the conclusion, FTIR absorption spectroscopy was used to determine the micro-

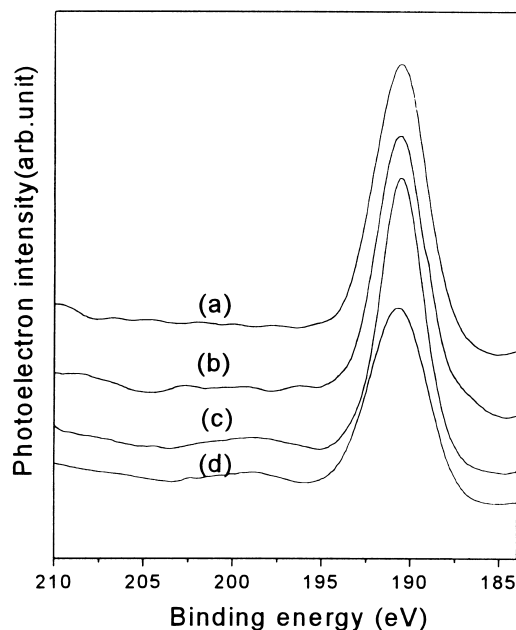


Fig. 3. B1s XPS spectra of BN film at different etching time (a) unetched; (b) 105, (c) 120, (d) 140 min.

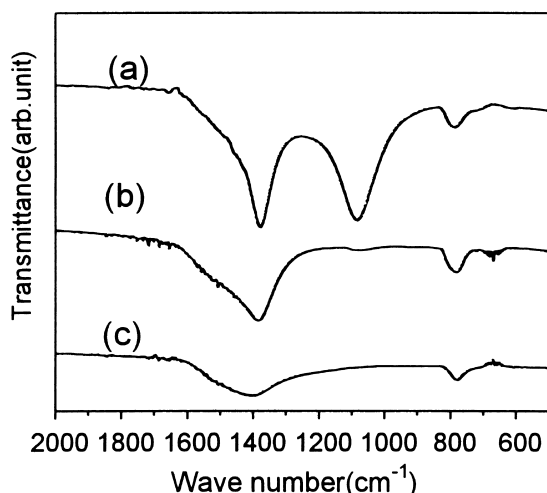


Fig. 4. FTIR spectroscopy of BN films measured at different etching time (a) 105, (b) 120, (c) 140 min

structure of BN film with different thickness at the etched region, as shown in Fig. 4. When the film was etched for 105 min, FTIR absorption spectra of the remaining BN film at the etched region shows a mixture of c-BN and h-BN phase (Fig. 4a), quite different from that of whole BN film, as shown in Fig. 1. When the film was etched for 120 min, FTIR exhibits a mostly h-BN phase in the remaining BN films at the etched region (Fig. 4b). At the interface close to the substrate, the peaks responding to h-BN phase became very weak due to very thin film (Fig. 4c). Fig. 6 shows the content of c-BN phase in remaining BN film at etched region estimated from the relative intensity of I_{1080} and I_{1360} peaks. Removal of the outer layer due to ion etching results in a decrease of content of c-BN phase in remained BN film. After etching for about 120 min, it reaches the h-BN region. The results of FTIR absorption spectroscopy and

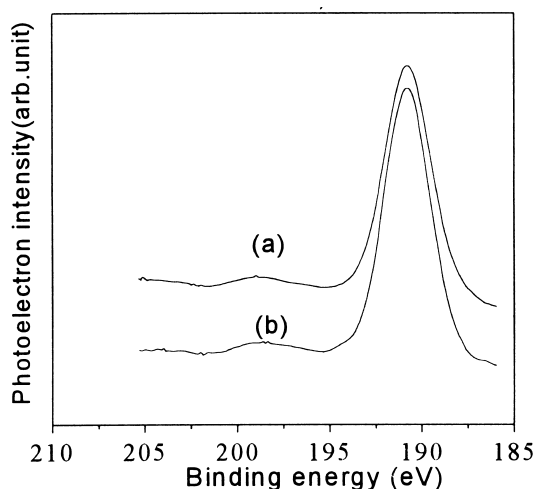


Fig. 5. B1s XPS spectra of pure h-BN film at different etching time (a) surface (b) 20 min.

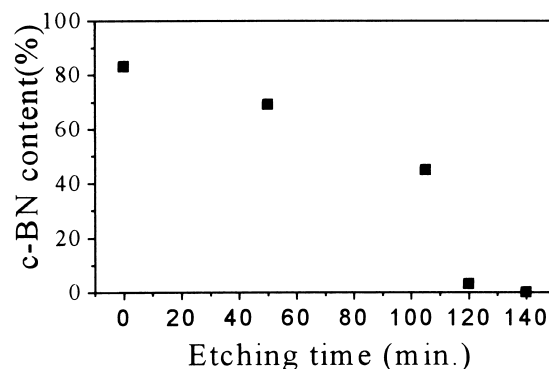


Fig. 6. c-BN content in remained BN film at etched region as a function of etching time.

B1s XPS spectra are clear evidences that the h-BN layer exists at the interface between the c-BN layer and the substrate. It is concluded that h-BN first grows prior to formation of c-BN.

A non-cubic phase existing at the interface was also confirmed by cross-sectional TEM micrograph, as shown in Fig. 7. A thin bright layer is observed at the interface, followed by a thick structured c-BN layer. Selected area diffraction patterns (SADP) taken at the top part of the layer shows continuous ring patterns (Fig. 8), which indicates that the film is polycrystalline. The measured interplanar spacings matched with those of bulk c-BN having lattice constant $a = 0.361$ nm within 1–2% error (Table 2). TEM results support the conclusion of FTIR and XPS, that a thin h-BN layer grows prior to the growth of the c-BN phase. It has also previously been reported that non-cubic phase (h-BN and or a-BN) appeared at the interface between c-BN layer and substrate through HRTEM cross-section observation of c-BN films deposited by other methods [8,9]. It is basically accepted that c-BN formation under low-pressure conditions is attributed to high compressive stress devel-

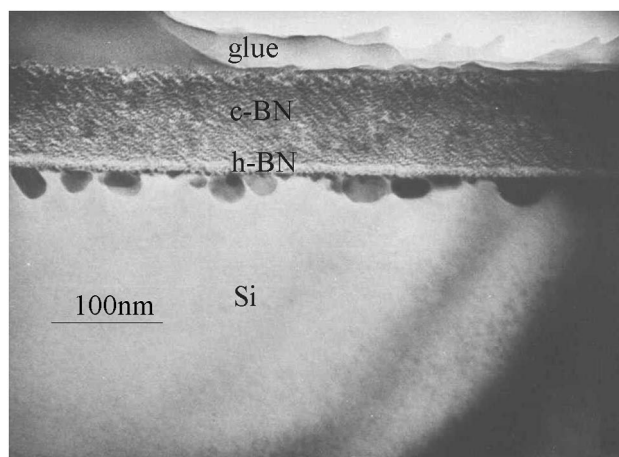


Fig. 7. Cross-section transmission electron micrograph of c-BN film deposited on Si(100).

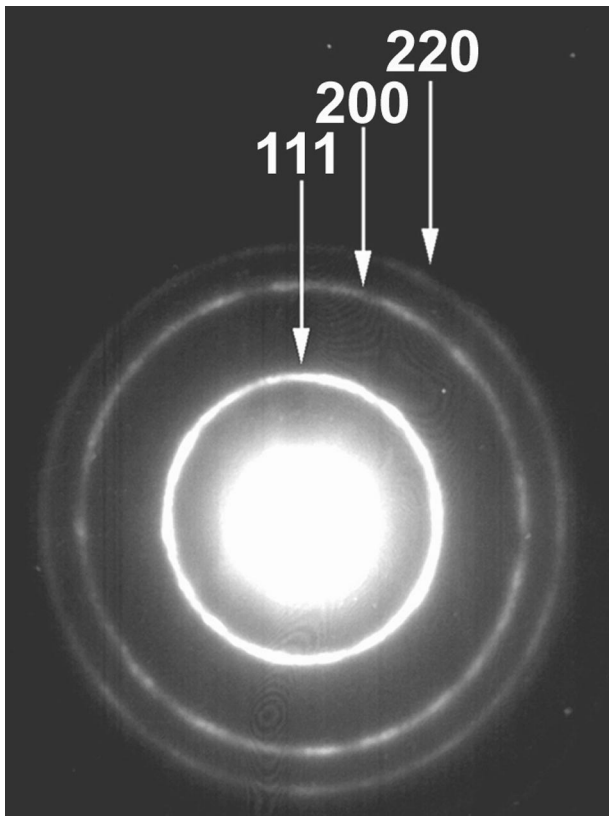


Fig. 8. Electron diffraction patterns taken from upper layer region of the film shown in Fig. 7

oped during BN growing due to ion bombardment [9]. 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.

Table 2

Measured interplanar spacing and standard spacings for ring pattern of c-BN specimen

Measured spacings		Standard spacings, d for c-BN	
d (Å)	(hkl)	d (Å)	(hkl)
2.073	(111)	2.088	(111)
1.798	(200)	1.808	(200)

4. Conclusion

A combination of XPS and FTIR absorption spectroscopy and TEM was used to characterize interfacial microstructure of c-BN film and substrate. It is found that h-BN phase first grows before c-BN phase started to grow, which is also consistent with the compressive stress induced formation mechanism of c-BN film.

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