ELSEVIER

Thin Solid Films 402 (2002) 117–120

thin solid films

www.elsevier.com/locate/tsf

Cubic BN formation by ion implantation

Cheng Hu[a,*], Q.M. Jonathan Wu[a], Jun Shen[a], Shigeo Kotake[b], Yasuyuki Suzuki[b]

[a]*National Research Council Innovation Centre, 3250 East Mall, Vancouver, BC, Canada V6T 1W5*
[b]*Department of Mechanical Engineering, Mie University, Tsu, Mie, Japan 514-8507*

Received 19 December 2000; received in revised form 23 July 2001; accepted 9 October 2001

Abstract

Boron nitride was synthesized by nitrogen ion implantation. Boron films were prepared as implantation targets on single-crystal Si(100) substrates by 13.56-MHz radio frequency sputtering. The diatomic single 30-keV nitrogen ions were chosen for implantation. The implantation dose ranged from 1×10^{17} ions/cm^2 to 2×10^{18} ions/cm^2. The films were characterized using a transmission electron microscope. Several phases of boron nitride were found at the medium implantation dose. At the high dose of 2×10^{18} ions/cm^2, the pure c-BN phase was observed. It is believed that the transition from the low ordered phases to c-BN phase occurred during implantation. The films showed good adhesion to the Si substrate.

Keywords: Boron nitride; Ion implantation; Transmission electron microscopy (TEM); Nitrogen

1. Introduction

The formation of cubic boron nitride (c-BN) films has attracted extensive research effort because c-BN shows excellent characteristics in mechanical, electronic and optical applications. Many successful c-BN film formations have been reported as physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques were employed. Ion bombardment of the film surface was considered crucial for c-BN synthesis during the film deposition process [1–4]. However, the formation of films with higher c-BN phase purity is still difficult. Some non-cubic BN phases tend to form before the c-BN is nucleated, which decreases the c-BN content in the film. The poor adherence of film to substrates was also a serious problem in many c-BN film formation experiments.

In this study, we demonstrate the synthesis of boron nitride by ion implantation. Several studies were performed in this area [5–7], but few of them reported c-BN formation. Compared with other ion assisted deposition techniques, ion implantation processes can avoid complications with the film growth process and the proportion of boron/nitrogen can easily be controlled over a large range. With a higher dose implantation, we expected to synthesize mainly c-BN films. Because the implantation layer is embedded in target films, the initial boron film between the implantation layer and the substrate can reduce the stress caused by c-BN formation. It is hopeful that the thick boron films can maintain their original good adherence with substrates after implantation.

2. Experimental

Boron films were prepared using a 13.56-MHz radio frequency (r.f.) sputtering on single-crystal Si(100) substrates. The film was deposited in an amorphous state to avoid the channeling effect during ion implantation. All films were grown to a thickness of approximately 1 μm, to obtain a boron layer sufficiently thick to reduce the stress caused by the implantation process.

* Corresponding author. Tel.: +1-604-221-3131; fax: +1-604-221-3001.
E-mail address: cheng.hu@nrc.ca (C. Hu).

0040-6090/02/$ - see front matter
PII: S0040-6090(01)01681-9

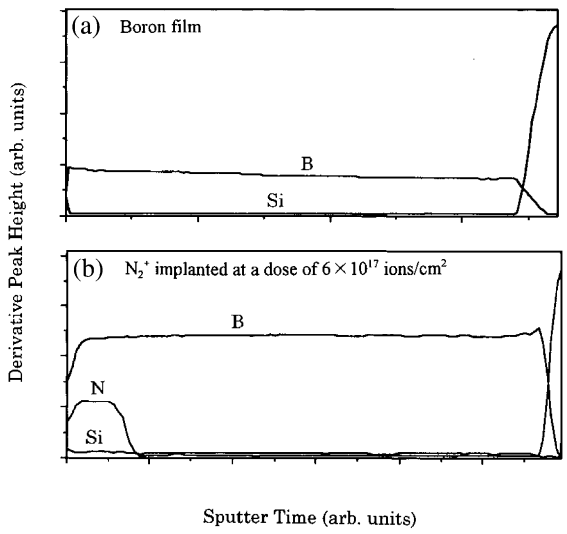

Fig. 1. Auger electron spectroscopy depth concentration profile: (a) before implantation and (b) after implantation at a dose of 6×10^{17} ions/cm^2.

The boron film under implantation layer can also avoid accumulation of charges during implantation. This experimental detail has been described in a former report [8].

The boron films were implanted in the target chamber of an ion implanter. Nitrogen gas was used to generate charged ions in a hollow-cathode-type ion source. In this experiment, only diatomic, single nitrogen ions, N_2^+, were selected for implantation by mass analysis. The ions were accelerated up to 30 keV. Boron films were implanted at doses ranging from 1×10^{17} ions/cm^2 to 2×10^{18} ions/cm^2. The ion beam current was monitored with a Faraday cup which surrounded the target. A properly irradiated area was chosen to maintain ion beam flux at 10 μA/cm^2. Implantation was carried out at room temperature. A thermocouple pressed directly to the substrate backside measured an approximately 20 K temperature increase in the samples during implantation.

To confirm the formation of BN in the implanted film, Auger electron spectroscopy (AES) was employed for the chemical composition analysis of as-sputtered boron films and ion-implanted films. An area on the films of 100 μm$\times$100 μm was etched with an argon ion beam. The microstructural identification of films was carried out using transmission electron microscopy (TEM) and transmission electron diffraction (TED) techniques on a JEOL H-9000 microscope.

2.1. TEM analysis

Because the BN implantation layer was buried in the boron film, it was difficult to identify the phase of the implanted samples by Fourier transform infrared transmission analysis (FTIR), which is widely used for c-BN identification. In this study, transmission electron microscopy (TEM) was employed as a main characterization technique to analyze the microstructure of films. AES chemical composition analysis was also carried out. Fig. 1 shows the AES result of the sample implanted at the dose of 6×10^{17} ions/cm^2. This confirmed that no impurities were misidentified as boron nitride.

Fig. 2 shows the TEM images of the as-sputtered boron film prior to implantation. The bright-field (a) and dark-field (b) images indicate that the film was in a nano-order clustered amorphous state. In the electron diffraction pattern (c), two dim halo-like rings corresponding to rhombohedral boron (100) and boron (211) implied low-order crystallization in the boron film. However, no notable crystalline particle was observed in the film.

Clear BN phases appeared after nitrogen ion implantation. Fig. 3 shows a TEM image of the films implanted at a dose of 6×10^{17} ions/cm^2. The crystals were distributed in the films without definite boundary or shape. The grains were estimated at 20–50 nm in diameter. Fig. 4 shows the TED pattern of the same film. The complicated diffraction pattern was proved to correspond to t-BN, c-BN, w-BN and tetragonal $B_{25}N$ (Table 1). The thick ring corresponding to a spacing of approximately 2.09 Å indicates some sort of fine structure, and is considered to represent c-BN(111) (2.088 Å) and w-BN(002) (2.114 Å). Tetragonal $B_{25}N$ was also found in some boron rich areas.

When the implantation dose was greatly increased, to 2×10^{18} ions/cm^2, the TEM image showed large grains filled with the film (Fig. 5a,b). Crystalline particles had grown as large as 40–100 nm, which were much bigger

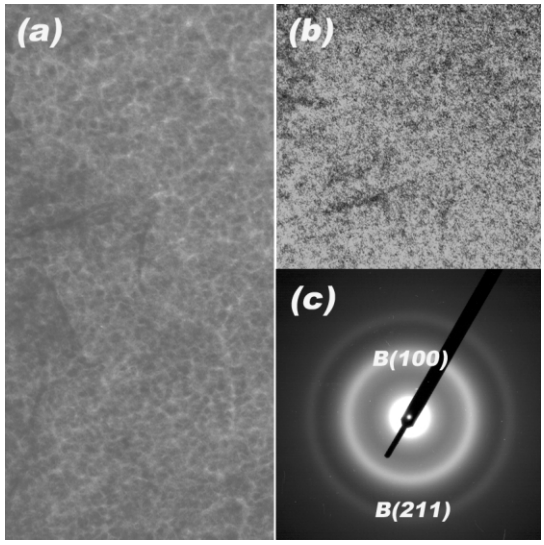

Fig. 2. TEM images of boron film before implantation: (a) bright-field image; (b) dark-field image; (c) TED pattern.

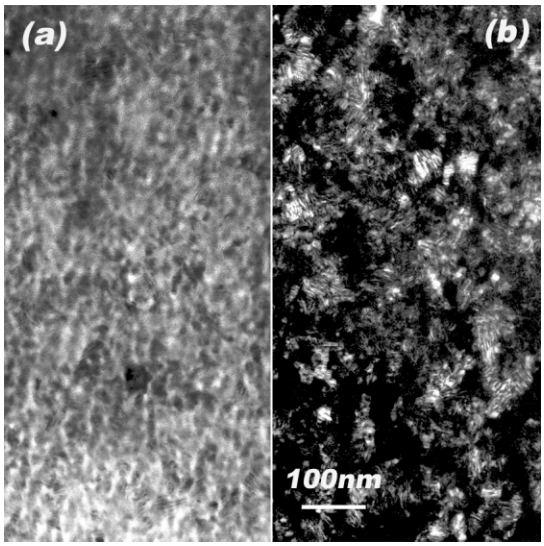

Fig. 3. TEM images of boron film implanted at a dose of 6×10^{17} ions/cm^2: (a) bright-field image; (b) dark-field image.

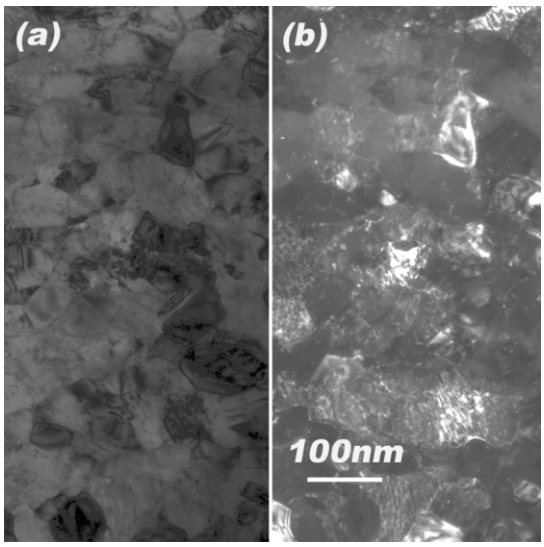

Fig. 5. TEM images of boron film implanted at a dose of 2×10^{18} ions/cm^2: (a) bright-field image; (b) dark-field image.

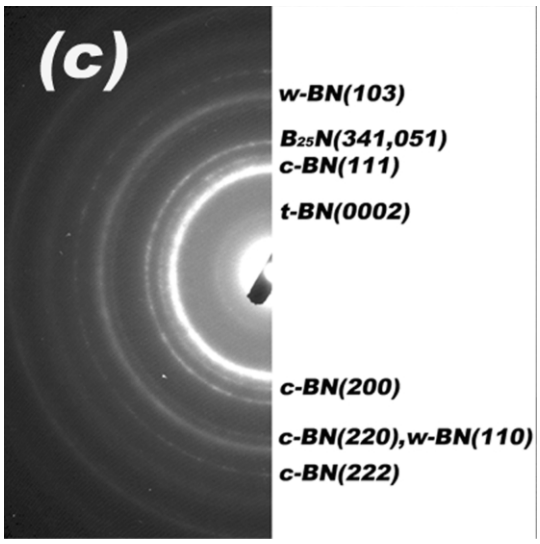

Fig. 4. TED pattern of boron film implanted at a dose of 6×10^{17} ions/cm^2.

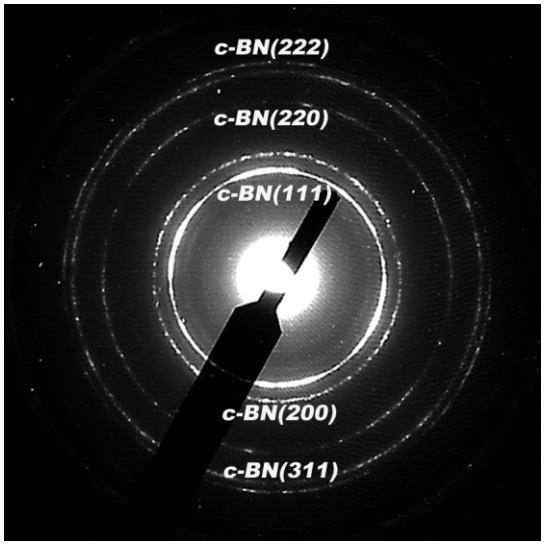

Fig. 6. TED pattern of boron film implanted at a dose of 2×10^{18} ions/cm^2.

Table 1
Diffraction data of boron film implanted at the dose of 6×10^{17} ions/cm^2 (Fig. 4) compared with reported data of c-BN

Observed data		c-BN		t-BN		w-BN		$B_{25}N$	
d (Å)	Intensity	*d* (Å)	*hkl*	*d* (Å)	*hkl*	*d* (Å)	*hkl*	*d* (Å)	*hkl*
3.50	Strong			3.56	0002				
2.09	Strong	2.088	111			2.114	002		
1.81	Medium	1.808	200						
1.64	Strong							1.6385	341,051
1.27	Weak	1.2785	220			1.277	110		
1.17	Weak					1.188	103		
1.04	Weak	1.0443	222						

Table 2
Diffraction data of boron film implanted at the dose of 2×10^{18} ions/cm^2 (Fig. 6) compared with reported data of c-BN

d (Å)		Intensity I/I_0			hkl
Sample	c-BN	Sample	c-BN(XRD)	c-BN(TED)	
2.09	2.088	Strong	100	100	111
1.80	1.808	Medium	0.8	2	200
1.28	1.2785	Medium	49	6	220
1.09	1.0901	Medium	26	3	311
1.04	1.0443	Medium	0.5	1	222

than the grains observed in the film implanted at a dose of 6×10^{17} ions/cm^2. The diffraction pattern corresponding to the same area shows that pure phase c-BN exists in the film (Fig. 6). The lattice spacings compared with reported data [9] are listed in Table 2. The contents of other BN phases in the film, such as t-BN, w-BN and $B_{25}N$, had decreased remarkably. Because the ion beam was maintained as a constant during implantation and these lower density phases (t-BN, w-BN and $B_{25}N$) were found plentiful in the film at the earlier stage of implantation, i.e. at medium dose implantation, this implies that phase transition occurred from lower density phases toward the c-BN phase. However, further research is needed to find direct evidence of the phase transition.

A similar experiment was also carried out on the lower ion energy of 20 keV. No c-BN phase was observed at implantation doses of 1×10^{17} ions/cm^2 to 2×10^{18} ions/cm^2. In this study, all films show good adhesion to the substrate after implantation. Boron films adhere with the substrate well before implantation. The implantation layer is too thin to affect the adhesion between the boron film and Si substrate. After implantation, no peeling was observed even during ultrasonic cleaning in the TEM sample preparation process. The main reason should be that the initial target boron layer greatly reduced stress between the c-BN layer and the Si substrate.

3. Conclusion

Boron nitride films were synthesized by the nitrogen ion implantation of boron films. It was found that c-BN could be synthesized with an ion energy of 30 keV and with implantation doses of beyond 6×10^{17} ions/cm^2. Under ion implantation, the c-BN phase could also be transited from the t-BN, w-BN and $B_{25}N$ phases. Increasing the implantation dose caused a corresponding increase in c-BN crystallization and a decrease in other lower density phase contents. At an implantation dose of 2×10^{18} ions/cm^2, a pure c-BN phase was observed in the film. The film showed good adhesion to the substrate after implantation.

Acknowledgements

The authors are very grateful to Dr Y. Takahashi of Mie University in Japan. His assistance with the TEM greatly helped.

References

[1] I. Jiménez, A. Jankowski, L.J. Terminello, J.A. Carlisle, D.G.J. Sutherland, G.L. Doll, J.V. Mantese, W.M. Tong, D.K. Shuh, F.J. Himpsel, Appl. Phys. Lett. 68 (1996) 2816–2818.
[2] O. Burat, D. Bouchier, V. Stambouli, G. Gautherin, J. Appl. Phys. 68 (1990) 2780.
[3] T. Wada, N. Yamashita, J. Vac. Sci. Technol. A 10 (1992) 515.
[4] D.J. Kester, R. Messier, J. Appl. Phys. 72 (1992) 504.
[5] L. Guzman, F. Marchetti, L. Calliari, I. Scotoni, F. Ferrari, Thin Solid Films 117 (1984) L63.
[6] T. Baazi, E.J. Knystautas, Thin Solid Films 232 (1993) 185.
[7] S. Kikkawa, H. Sugiyama, F. Kanamaru, J. Mater. Sci. Lett. 16 (1997) 1151–1152.
[8] C. Hu, S. Kotake, Y. Suzuki, M. Senoo, Jpn. J. Appl. Phys. 38 (1999) 6054.
[9] P.B. Mirkarimi, K.F. McCarty, D.L. Medlin, Mater. Sci. Eng. R 21 (1997) 47.