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# MODIFICATION OF INITIALLY GROWN BN LAYERS BY POST-$N^+$ IMPLANTATION

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## Abstract

BN films with a high content of cubic phase has been deposited by a variety of techniques. It is well known that c-BN films grow with a unique microstructure consisting of $sp^2$ and $sp^3$-bonded layers. Because of existence of the initially grown $sp^2$-bonded layer, BN films are not adhesive to the substrates. In this study, post-$N^+$ implantation was applied to improve the adhesion of the films. A Monte Carlo program TAMIX was used to simulate this modification process. The simulation showed nitrogen concentration profile at 1200Å in depth in case of 50keV-implantation energy. FTIR spectra of the $N^+$ implanted specimens demonstrated a strong change of absorption band at 1380 $cm^{-1}$. The films were also investigated by HRTEM. From these results, it is concluded that the post ion implantation could be an effective technique which improves the adhesion between BN film and substrate.

***Key words*** : *cubic boron nitride, post-ion implantation, interfacial structure, HRTEM, adhesion.*

## 1. INTRODUCTION

Recently, synthesis of cubic boron nitride (c-BN or cBN) films has been stimulated by its unique physical and chemical properties : extreme hardness, excellent chemical inertness, thermal stability, wide band gap and good optical transparency in a wide range of wavelength. The combination of high hardness with a high temperature oxidation resistance to ferrous-based materials is favorable for future tribological and protective applications.[1)]

BN films with a high content of cubic phase can now be routinely deposited by a variety of techniques. In addition, progress has been made in understanding how energetic deposition conditions can lead to c-BN formation.[2)] It is generally known that c-BN films grow with a unique microstructure consisting of $sp^2$ and $sp^3$-bonded materials.[3)] Because of existence of the initially grown $sp^2$-bonded layer, c-BN films delaminate easily from the substrates. This has been one of the major limiting factors of using the c-BN films for many important applications such as cutting tools.[4)]

In this experiment, post-ion implantation has been applied to improve the adhesion of the films. Ion implantation is the process of accelerating $N^+$ ions to a high velocity, directing them into materials, especially, weak $sp^2$-bonded layers and thereby altering the chemical composition, microstructure and/or stress conditions. The effect of ion implantation on microstructure was investigated using FTIR and transmission electron microscopy and microhardness was measured.

## 2. EXPERIMENTAL

Boron nitride films were deposited on (100)-oriented Si substrates by magnetically ehanced-activated reactive evaporation (ME-ARE) method. A detailed description of this ME-ARE is given elsewhere[5, 6)]. A highly optimized dynamic Monte Carlo program TAMIX[7)] was used on the Cray supercomputer to simulate this modification process. According to this simulation, ion implantations were conducted at 50kV with several ion doses on BN films.

## 3. RESULTS AND DISCUSSION

Fig. 1 shows a high resolution lattice image obtained from the c-BN samples. The image shows that the interfacial layer contains two regions. The first region next to the substrate has a highly disordered structure with small patches of lattice fringe, this fringes followed by the region with fringes lie in parallel lines. The disordered region is believed to be an amorphous BN and the parallel fringe region is similar to hexagonal or turbostratic BN. The top layer consists of randomly oriented c-BN crystallites. Fast Fourier Transform (FFT) was performed on each layer and the images are given in the insets of photographs. FFT images confirmed the observed HRTEM results. A part of the c-BN (111) ring and the ring corresponded to (002) h-BN are shown in FFT images.

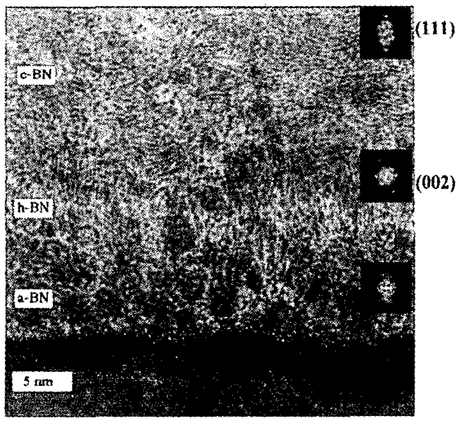

Fig. 1 HRTEM cross-sectional micrograph of c-BN film

In order to modify this intrinsic layer, post-ion implantation was applied. Prior to implantation, a highly optimized dynamic Monte Carlo program TAMIX was used to simulate this modification process. Fig. 2 is a TAMIX simulation results of nitrogen ion implantation on c-BN/h-BN/Si layered structure. As shown in the Figure, the implantation at 50kV made more atomic displacements at the interface. According to this simulation, post-ion implantation was conducted at 50kV with $1\times10^{15}\sim2\times10^{16}$ doses.

FT-IR spectra of BN films with 27% cubic phase before and after implantation are shown in Fig. 3. As the ion dose increased, the charac-

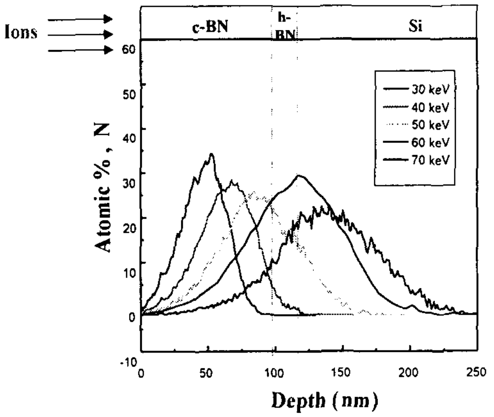


Fig. 2 TAMIX simulation of $N^+$ on c-BN/h-BN/Si.

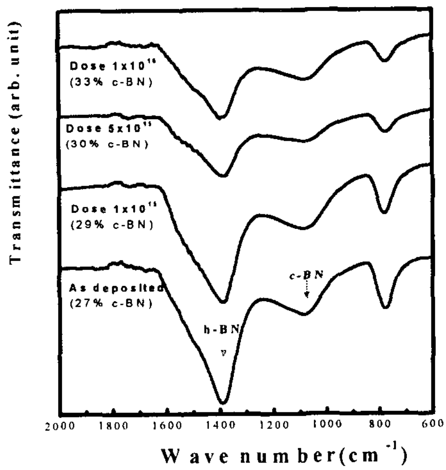


Fig. 3 Variation of FTIR spectra of c-BN by $N^+$ implantation.

teristic absorption band of h-BN was gradually reduced, but that of c-BN did not changed apparently. Similar results, not shown here, were observed for the BN films with 60% and 90% cubic phase. This suggests that the nitrogen implantation created some displacements of atoms of the c-BN and h-BN phases.

To study the effect of ion implantation on microstructure, the cross-sectional HRTEM images were taken on ion implanted films. The image of the as-deposited sample shows a diffuse interfacial layer of amorphous phase followed by a hexagonal layer, while that of the ion implanted film at 50kV apparently shows the directional feature of film structures as shown in Fig. 4. The small crystallites with horizontally spaced fringes has turned into those with vertical fringes (marked arrows). It seems that the ion irradiation caused the recrystallization of amorphous phase and transformed the small crystallites to other phase. Hexagonal BN layer also seems to be have been disturbed by ion implantation and revealed a mixture of both h-BN and turbostratic BN features. These microstructural changes were confirmed by FFT of high resolution images. This suggest that some atomic displacement induced by ion implantation on the interfacial layer resulted interlocked interface and thereby could improve the adhesion of the film.

In order to identify this suggestion, BN samples as-deposited and implanted with various ion dose were placed in the air for a month. Film delamination was detected by visual inspe-

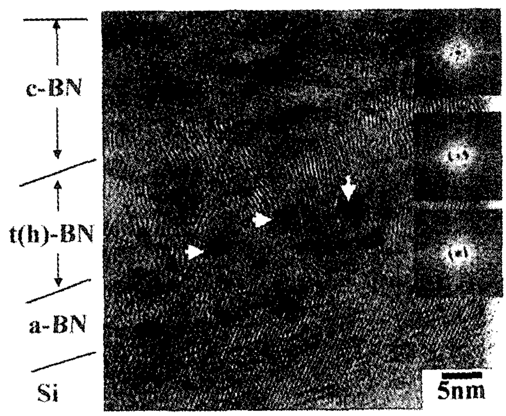


Fig. 4 HRTEM images of c-BN films after $N^+$ implantation.

ction at time intervals and are shown in Fig. 5. In this figure, as-deposited and implanted samples with low ion dose delaminated after few days. However, no sign of delamination for the samples implanted with a dose range of $1\times16^{16}$ $\sim 2\times10^{16}$were observed.

Fig. 6 shows the effect of ion implantation dose on microhardness of BN films. Microhardness was measured at a load of 0.05g. As content of cubic phase in the as-deposited BN films increased from 27% to 60%, the microhardness increased from 800 up to 3800. It is noted that the ion implantation with low ion doses did not give any rise to microhardness regardless of the content of cubic phase. A drastical increase in microhardness was observed in case of a high ion dose of $1\sim2\times10^{16}$ ions /cm$^2$ The BN film with the 60% cubic phase demonstrated a microhardness as high as 6000 afterion implantation with a high dose of $2\times10^{16}$ ions/cm$^2$, which is in the range of microhardness of bulk c-BN materials, 4700~8600.

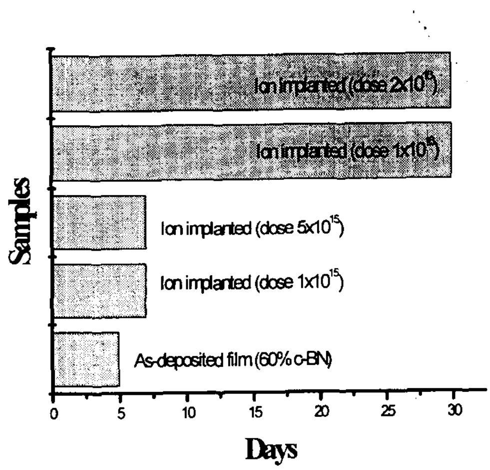


Fig. 5 Effect of ion dose on delamination time of BN films with 60% cubic content.

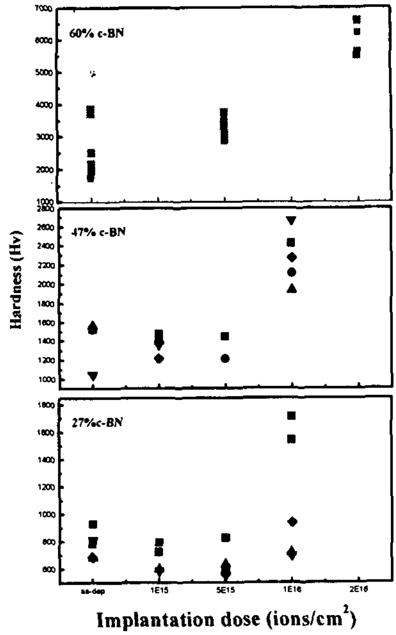


Fig. 6 Microhardness of BN films as a function of c-BN content and ion dose(Load : 0.05g)

## 4. CONCLUSIONS

Post $N^+$ implantation was proved to be an effective technique which could improve the properties of c-BN films. At an optimal implantation condition, an acceleration voltage of 50kV and an ion dose of $2\times10^{16}$ ions/cm$^2$ in this study, microhardness and delamination life time of the c-BN films were significantly improved. This is belived to have been caused by atomic displacements in the initially grown amorphous and hexagonal layers, which were confirmed by a HRTEM microstructural observation.

## 5. ACKNOWLEDGMENTS

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