mM), $Co(NO_3)_2$ (0.2 mM), and $KHSO_5$ (10 mM). The reaction solution was analyzed by LC/MS.
9. ^{16}O and ^{18}O compositions in CBZ-oxide product were determined by the relative abundances of mass peaks at m/z=253 for ^{16}O and m/z=255 for ^{18}O.
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13. A solvent mixture (5 mL) containing 50% H_2O, 40% CH_3CN, and 10% CH_3OH was used to make the reaction solution homogeneous. Reaction conditions were the same as for the CBZ epoxidation reaction except that $Co(NO_3)_2$ (0.2 mM) and *cis*-stilbene (10 mM) were used. *cis*-Stilene oxide (0.9 mM), *trans*-stilbene oxide (0.11 mM), and benzaldehyde (0.08 mM) were found to be formed as products in this reaction.
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Optical Time-of-Flight Studies on the Laser Ablation of Boron Nitride

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Received February 5, 1996

The laser ablation of solid targets has been a research topic of interest since the invention of lasers. With developments of high power lasers in the ultraviolet region, deposition of thin films by laser ablation has been extensively studied aiming at the growth of high quality films of different types including superconductors, semiconductors, ferroelectrics, and dielectrics.[1] In particular, laser ablation technique has been proved to be especially powerful in the stoichiometric deposition of multi-element materials like YBCO superconductors.[2] Currently, deposition of thin films by laser reactive ablation is emerging, where laser ablation occurs under reactive gas environment. This technique has been applied to the deposition of refractory nitride materials such as boron nitride,[3a] silicon nitride,[3b] and carbon nitride.[3c]

In this communication, we report experimental results on the optical time-of-flight (TOF) studies of laser ablation of pyrolytic boron nitride (pBN, Union Carbide) in nitrogen. This is the first optical TOF study of BN laser ablation to our knowledge. The laser ablation of BN has been done by several groups with a goal to deposit epitaxial cubic boron nitride (cBN) thin films.[4] cBN is one of the most promising materials with diverse applications in electronics, optics, and hard coatings.[5] The efforts to deposit epitaxial cBN films by laser ablation, however, were not successful presumably due to the deficiency of detailed information on the laser ablation dynamics.

The quality and properties of films deposited by laser ablation are expected to be highly dependent on the characteristics of the plume generated in laser ablation process. The information on the formation and evolution of laser-induced plume from the target and the transport of the ablated species to the substrate will be of critical importance in understanding the dynamics involved in the pulsed laser deposition of materials. So far several methods including probe beam deflection,[6] laser-induced fluorescence,[7] time-of-flight,[8] optical time-of-flight,[9] resonance absorption,[10] resonance ionization,[11] and ultrafast photography[12] have been employed to diagnose the plume in laser ablation. Among these methods, optical TOF technique has its unique features in that it can measure the dynamic properties of chemical species including both neutrals and ions with spectral resolution *in situ*, where the ambient pressure is often too high for a TOF or quadrupole mass spectrometer to be used.

In this work, we have adopted optical TOF technique to investigate the velocity and concentration of the species produced in the laser ablation of pBN. The laser ablation of pBN was done by the fourth harmonic of Nd : YAG laser (266 nm, Quanta-Ray GCR 150) with pulse duration of 5 ns operating at 10 Hz. The experimental setup is shown in Figure 1. Briefly, the Nd : YAG laser beam was focused onto the pBN target by a S1UV lens with focal length of 20 cm. Optical emission from the plume generated by the laser ablation was imaged into an optical fiber by a lens (f=3.7) and fed to a monochromator (SPEX 500M) equipped with a photomultiplier. The photomultiplier signal was averaged and stored in a digital storage oscilloscope (LeCroy 9304, 175 MHz). The emission spectrum was also obtained with the monochromator, where a boxcar averager (PAR 162) was employed for signal processing. Vibrational progressions from molecular BN transition ($A^3\Pi \rightarrow X^3\Pi$) as well as emissions from the excited B atoms and B^+ ions were also obser-

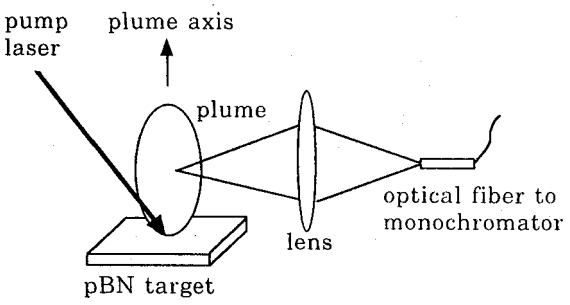

Figure 1. The experimental setup for optical TOF studies of laser ablation. The lens was mounted on a 3-dim. translational stage.

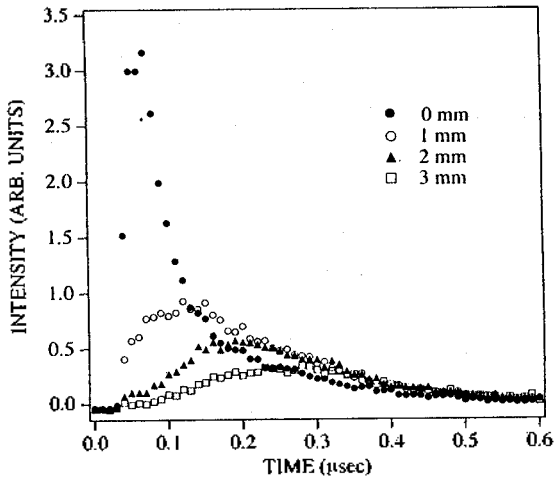

Figure 2. The optical TOF signals from B atoms at different probe positions. Laser fluence was 12 J/cm^2 and the nitrogen pressure was 100 mTorr.

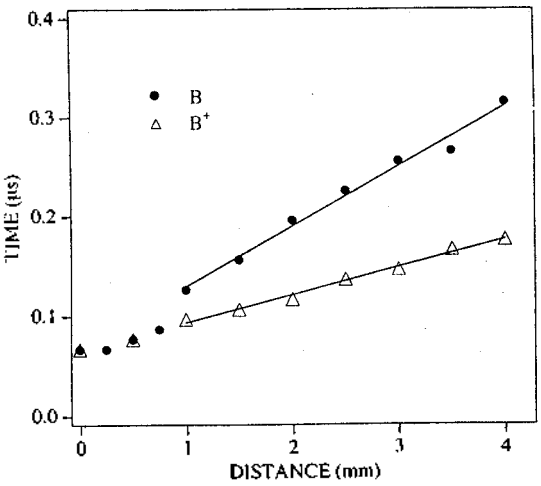

Figure 3. Time delay between the laser pulse and the emission maximum as a function of the probe position along the plume axis for B atoms and B^+ ions. Laser fluence was 12 J/cm^2 and the nitrogen pressure was 100 mTorr.

ved when the optical fiber probe was positioned near the target (from 0 to 1 mm). The emissions from N atoms and N^- ions were not strong enough for optical TOF studies, hidden under molecular emissions, if any.

Figure 2 shows the real time emission intensities at 249.7 nm from the B 3s(1/2)→2p(1/2, 3/2) atomic emission line at different distances along the plume axis. The time delay between the ablation laser pulse and the emission intensity maximum at different probe positions are shown in Figure 3, where the inverse of the line slope is the most probable velocity of the corresponding species.[9] The emission from B^+ ions was measured at 345.1 nm of 2p(0)→2s(1) transition. The most probable velocities thus obtained indicate that B^+ ion is much faster than B atom at distances longer than 1 mm. Due to the Coulomb attraction of ions by electrons that nearly escape at the plume boundary producing a space charge field, ions are accelerated according to their charge.[13]

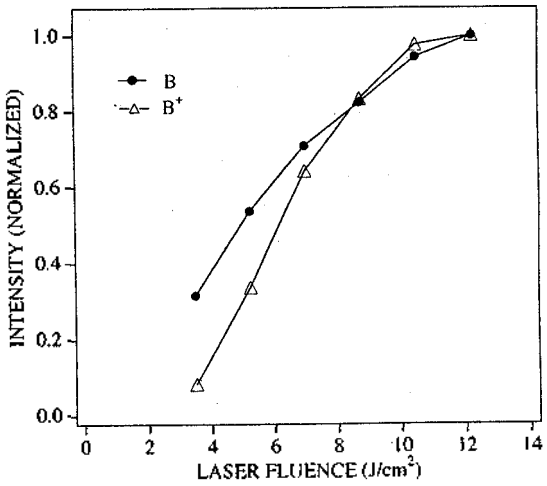

Figure 4. The emission intensity vs. laser fluence for B atoms and B^+ ions. The probe position was 0.25 mm from target along the plume axis. The nitrogen pressure was 100 mTorr.

The most probable velocities of B atoms and B^+ ions as measured at distances longer than 1 mm were 1.7×10^6 cm/sec and 3.6×10^6 cm/sec, respectively. The velocity of B atoms, however, was nearly the same as that of B^+ ions at distances shorter than 1 mm from the target as in the case of laser ablation of Ge.[9] These fast neutrals can be identified as ions recombining with electrons, implying that the earlier species in the plume are mainly charged species.

The most probable velocity of B atoms near the target (from 0 to 1 mm) increased as the laser fluence increased. At distances longer than 1 mm, there was no appreciable trend observed in the effect of laser fluence on the velocity of B atoms. The velocity of ions, however, increased with laser fluence at distances up to 4 mm away from the target. This results indicate that the expansion of species in laser ablation can not be understood with simple kinetic concept.

The ion-to-neutral population as measured from the emission intensities of B^+ ions and B atoms increased by a factor of up to 2.6 times as the laser fluence was increased from 3.5 to 12 J/cm^2 as shown in Figure 4. According to the Saha equation[14] which predicts the ratio of singly charged ions to neutrals in the plume under local thermodynamic equilibrium, relative increase of ion signal implies the increase of the plume temperature. Enhancement of ion bombardment during BN film growth is thus expected with increase of laser fluence in the fluence range of this experiment.

In summary, we have studied the laser ablation of pBN by optical TOF method which enabled the derivation of velocities of ions and neutrals produced under deposition condition. Also obtained was the effect of laser fluence on the relative concentrations of ions and neutrals. The effect of relative concentrations and kinetic energies of chemical species in the plume on the properties of BN films deposited under different ablation conditions will be studied in the future.

Acknowledgment. This work was supported by the Korea Science and Engineering Foundation (Grant No. 95-0501-09-01-3) SMP is also grateful to Research Institute for Basic Sciences, Kyung Hee University (University Resear-

ch Fund, 1996) and Basic Science Research Institute Program, Ministry of Education (Project No. BSRI-95-6401).

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