Extended Abstracts of the 17th Conference on Solid State Devices and Materials, Tokyo, 1985, pp. 169-172



# Laser-Assisted Chemical Vapor Deposition of Stoichiometric Boron Nitride

Shin Yokoyama, Yasuhiro Yamakage and Masataka Hirose
Department of Electrical Engineering, Hiroshima University
Higashihiroshima 724, Japan

Nearly stoichiometric boron nitride films were deposited by ArF excimer laser irradiation in a $B_2H_6$+$NH_3$ gas mixture at substrate temperatures between 300 and 400 °C. The deposition rate is decreased by the laser irradiation, because of a change in the growth kinetics by photo-irradiation, as evidenced by the fact that the activation energies of the deposition rate for thermal and laser-assisted chemical vapor deposition (CVD) are 1.9 and 2.5 eV, respectively. The compositional ratio N/B or stoichiometry evaluated by X-ray photoelectron spectroscopy was found to be dramatically improved with the laser irradiation.

## Introduction

Boron nitride (BN) is chemically stable and could be utilized as an interlayer dielectric film between metallization levels because of the large thermal conductivity and high resistivity.[1)] Boron nitride has so far been prepared by the pyrolytic or glow discharge decomposition of $B_2H_6$+$NH_3$[1-4)] or $BCl_3$+$NH_3$.[5)] In the thermal CVD a stoichiometric film is not prepared at low temperatures,[4)] while in the plasma CVD nearly stoichiometric BN is obtainable even at 300 °C.[1)] Photochemical deposition of BN film is another candidate of low temperature processes and has an advantage as a silent process which enables us to avoid the ion bombardment damage in the plasma deposition.

In this paper, boron nitride deposition has been carried out at temperatures 300 to 400 °C with and without ArF excimer laser irradiation, and the influence of the laser irradiation on the chemical natures of the deposits is examined by X-ray photoelectron spectroscopy (XPS) and infrared (ir) absorption measurements.

## Experimental

A schematic diagram of experimental apparatus is shown in Fig. 1, where ArF excimer laser (Lambda Physik EMG 103E) light (193 nm in wavelength) with pulse energies of 5-26 $mJ \cdot cm^{-2}$

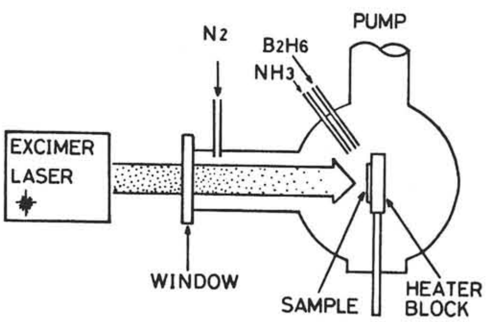


Fig. 1 Schematic diagram of experimental apparatus.

/shot at a repetition rate of 80 pps was irradiated onto a Si wafer held in a $B_2H_6$+$NH_3$ gas mixture. The light intensity was controlled by the supplied voltage to a thyratron connected to the discharge electrode of the laser. Substrate temperature, pressure, flow rate of $B_2H_6$ diluted to 11 % with $H_2$ and of $NH_3$ diluted to 14.7 % with $H_2$ are, respectively, 300-400 °C, 10 Torr, 1-20 sccm, and 50 sccm. BN deposition inside of the quartz window was avoided by blowing nitrogen gas onto the internal surface of the window. The chemical bonding features and compositions of the deposits were analyzed by XPS (Shimadzu ESCA 750H).

## Results and Discussion

The deposition rate of BN films produced by the thermal and laser-assisted chemical vapor

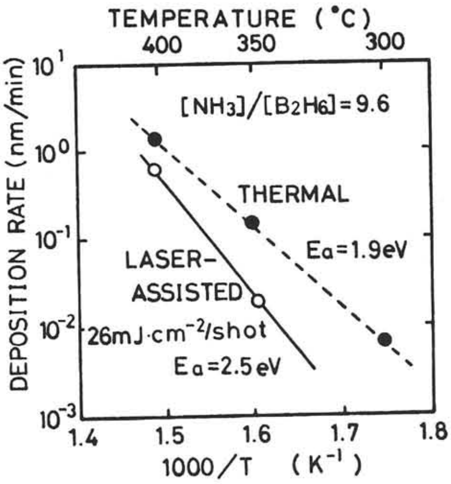


Fig. 2 Deposition rate of BN films as a function of reciprocal temperature for thermal and laser-assisted CVD. The thickness of the film was evaluated by the ellipsometry, and cross-checked by the Ar ion sputtering time to etch out the deposited film, and estimated by the XPS signal intensity ratio of Si(2p) from Si substrate to N(1s) from BN film.

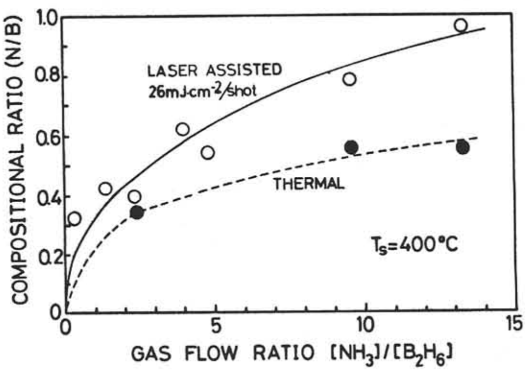


Fig. 3 The compositional ratio N/B as a function of gas flow ratio $[NH_3]/[B_2H_6]$ for thermal and laser-assisted CVD films. Laser output power is 26 $mJ \cdot cm^{-2}$/shot and the substrate temperature is 400 °C.

deposition was measured as a function of reciprocal temperature as shown in Fig. 2. BN films can be thermally grown at temperatures above 300 °C with an activation energy of 1.9 eV, which is largely different from 0.48 eV obtained by Adams et al.[4] They adopted very small flow ratio of $NH_3$ to $B_2H_6$ being near unity and hence a boron-rich film must be obtained. This would be a possible reason of the low activation energy. The laser irradiation reduces the deposition rate by a factor 2 to 10, and the activation energy is increased to 2.5 eV. It is likely that collisional reactions of radicals produced by the photochemical decomposition of $B_2H_6$ and $NH_3$ result in the formation of gas phase intermediates such as aminoborane containing $-NH_2BH_2-$ chains,[6] and the activation energy for promoting the surface reactions of adsorbed precursors created from such polymer becomes large compared to that for the thermal reactions of radicals created from $B_2H_6$ and $NH_3$ on the surface. As stated above the compositional ratio of nitrogen to boron N/B for thermal and laser-assisted CVD films is strongly dependent on the flow ratio of $NH_3$ to $B_2H_6$ $[NH_3]/[B_2H_6]$. The compositional ratio determined from the XPS spectra by using the photo-ionization cross sections of boron and nitrogen atoms is shown in Fig. 3. Note that the laser irradiation improves the N/B ratio. At a flow ratio of 13.4, N/B=0.5 (boron rich) for a thermally grown film is increased to near unity (stoichiometry) for a film with laser irradiation. The saturated compositional ratio of thermally grown films can not reach unity at a deposition temperature of 400 °C. That is, the stoichiometric film can not be synthesized by the thermal CVD alone at such a low temperature because the thermal dissociation rate of $B_2H_6$ is considerably larger than that of $NH_3$ at temperatures around 400 °C.[3] A significant improvement of the N/B ratio by the laser irradiation at high flow ratios is ascribed to the fact that the photo-dissociation rate of $B_2H_6$ is 4 times larger than that of $NH_3$ at 193 nm.[7,8] As shown in Fig. 4, the XPS spectrum of the thermal CVD film exhibits B(1s) peaks at 188 eV due to metallic B-B bond and at 191 eV arising from B-N bond. In contrast to this, the laser-assisted CVD film represents the spectrum composed of a single B(1s) peak at 191 eV. It is clear that the ArF excimer laser irradiation dramatically improves the stoichiometry of BN films because nitrogen radicals in the gas phase are increased by laser irradiation and because 193 nm photons break the B-B bonds not only in gas phase but also on the growing film surface. Further difference between thermal and laser-assisted CVD films is observed in Fig. 5. The infrared absorption due to the BH stretching mode at 2450 $cm^{-1}$ in the thermal CVD

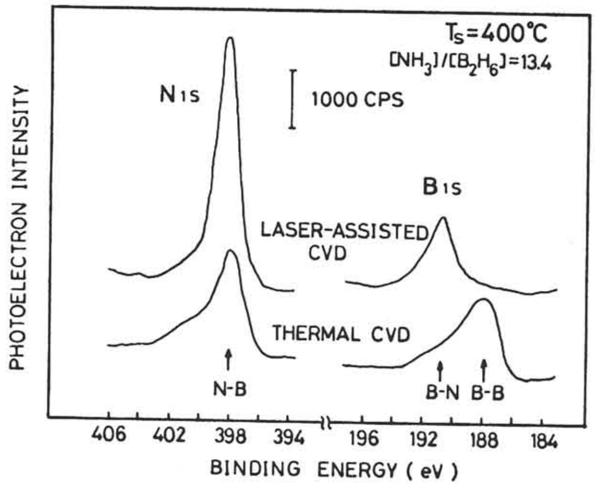


Fig. 4 The XPS spectra for the thermal and laser-assisted CVD boron nitride films.

film is eliminated in the laser-assisted sample. It is interesting to note that in plasma CVD the BH stretching absorption is also quenched when the stoichiometry of BN film is satisfied.[1] And, the infrared absorption peak due to the BN bond at 1350 $cm^{-1}$, which is assigned as in-plane vibration of locally hexagonal BN network, becomes sharp by the laser irradiation. This implies that the short range order of the BN network becomes more homogeneous by the laser

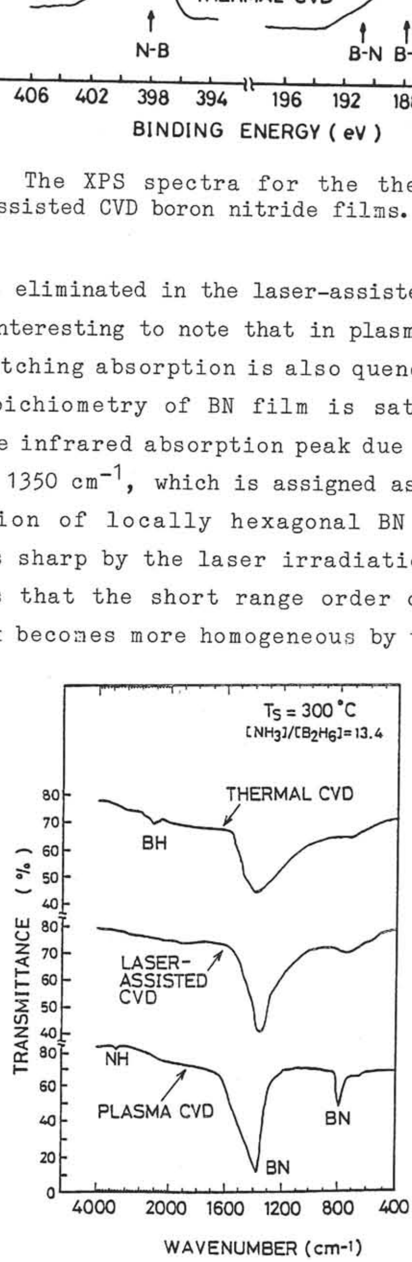


Fig. 5 The ir absorptiion spectra for the thermal and laser-assisted CVD boron nitride films. BN absorption at 800 $cm^{-1}$ is due to out-of plane vibration of hexagonal BN, while 1350 $cm^{-1}$ absorption is due to in-plane mode. The ir absorption spectrum for a plasma CVD BN film grown at a flow ratio $[NH_3]/[B_2H_6]$ of 16 is also indicated as a reference.

irradiation partly due to removal of BH bonds in the network. The absorption at 800 $cm^{-1}$ is sharp in the plasma CVD sample compared with that in tha laser-assisted film because of the difference in the film thicknesses.

Figure 6 (a) represents the deposition rate and refractive index of the laser-assisted CVD films as a function of laser pulse energy. The deposition rate tends to saturate at high laser power. This is primarily explained by a change in the deposition kinetics under laser irradiation (see Fig. 1). If it is assumed that the gas phase intermediate such as aminoborane is one of film precursors, laser ablation of such polymeric adsorbate on the deposition surface will also reduce the growth rate. Efficient removal of the polymeric species as well as B-B bonds on the surface under laser irradiation results in a decrease of the refractive index. In Fig. 6 (a) the gas flow ratio $[NH_3]/[B_2H_6]$=9.6

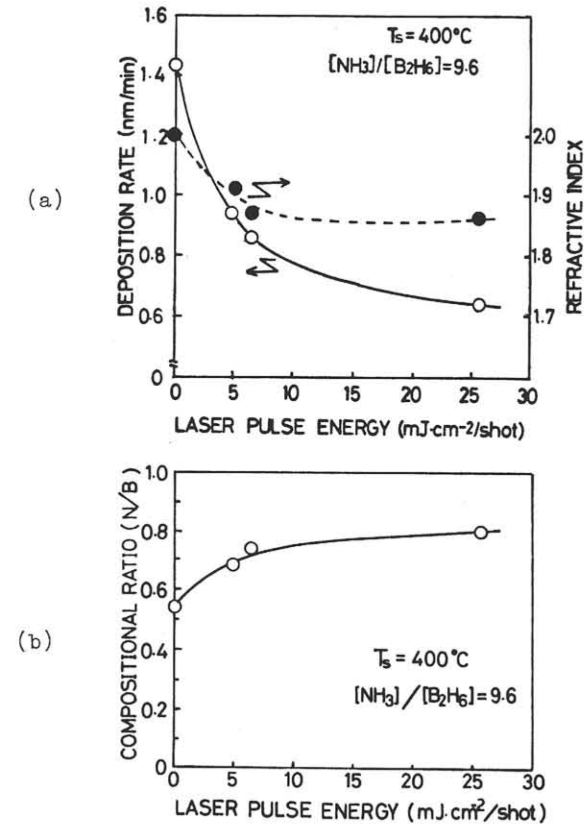


Fig. 6 (a) Deposition rate and refractive index of the thermal and laser-assisted CVD boron nitride as a function of laser pulse energy. (b) The compositional ratio N/B for laser-assisted CVD boron nitride as a function of laser pulse energy.

is not large enough to obtain stoichiometric BN with a refractive index of 1.75[1] even at high laser power as understood from the result of Fig. 3. Figure 6 (b) shows the laser power dependence of the compositional ratio N/B again at a gas flow ratio of 9.6. With increasing the laser power the composional ratio is increased from 0.55 to 0.8. The saturated N/B ratio is not equal to unity again, because the flow ratio is not large enough.

For the purpose of characterizing the electronic properties of BN films, Al/BN/n-Si structures were fabricated. The leakage current of the MIS structure utilizing a laser-assisted BN film is significantly low compared with that using a thermal BN film. This correspopnds to the extent of stoichiometry of the deposits. Figure 7 shows the C-V curves for an MIS structure with a laser-assisted BN film as an insulator. The ion-drift type hysterisis of the C-V curve arising from surface contamination in the reactor is not shown here to avoid complexity. The minimum interface trap level density evaluated from the quasi-static C-V curve is also high compared with that for the plasma CVD BN,[1] in which hydrogen plasma pretreatment of the Si surface was carried out to remove the native oxide. When the native oxide is removed by photochemical etching using $NF_3$[9] or $Cl_2$[10,11] before the laser-assisted deposition of BN, the interface properties could be significantly improved.

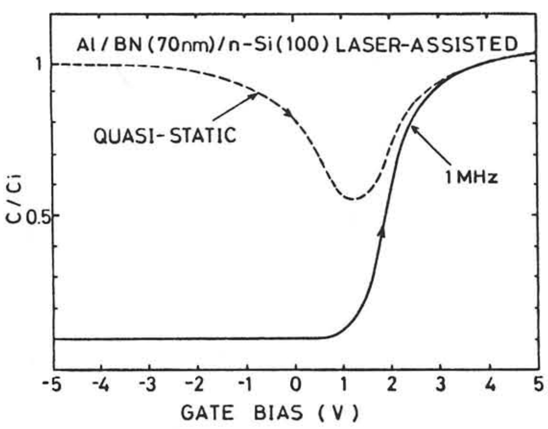


Fig. 7 Quasi-static and 1 MHz C-V curves for Al/laser-assisted CVD BN (70 nm in thickness)/n-Si(100) structure. Growth condition of BN film is same as in Fig. 6. Sweep rate of the ramp voltage is 50 mV/sec.

In conclusion, it is demonstrated that stoichiometric BN with homogeneous short range order has been grown by laser-assisted CVD from $B_2H_6$+$NH_3$.

References


1) H. Miyamoto, M. Hirose and Y. Osaka: Jpn. J. Appl. Phys. 22 (1983) L216.
2) M. J. Rand and J. F. Roberts: J. Electrochem. Soc. 115 (1968) 423.
3) S. P. Murarka, C. C. Chang, D. N. K. Wang and T. E. Smith: J. Electrochem. Soc. 126 (1979) 1951.
4) A. C. Adams: Technical Notes of J. Electrochem. Soc. 128 (1981) 1378.
5) H. Hannache and R. Naslain: Journal of the Less-Common Metals, 95 (1983) 221.
6) R. A. Geanangel and J. W. Rabalais: Inorganica Chimica Acta. 97 (1985) 59.
7) E. Tannenbaum, E. M. Coffin and A. J. Harrison: J. Chem. Phys. 21 (1953) 311.
8) W. Fuss: "On the orbital sequences in simple boron compounds", Dissertation, J. W. Goethe Univ., Frankfort (1971).
9) S. Yokoyama, Y. Yamakage and M. Hirose: Appl. Phys Lett. 46 No. 8 (1985) to be published.
10) D. J. Ehrlich, R. M. Osgood, Jr. and T. F. Deutsch: Appl. Phys. Lett. 38 (1981) 1018.
11) Y. Horiike, M. Sekine, K. Horioka, T. Arikado and H. Okano: Extended Abstracts of the 16th (1984 International) Conference on Solid State Devices and Materials, Kobe, 1984, p. 441.