# EXPERIMENTAL STUDY ON REDUCTION
# OF HYDROGEN CONTENT IN LOW Z THIN FILMS BY
# CONTROLLING DC GLOW DISCHARGE CONDITIONS

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*Dedicated*
*To my family, Yenni westi (wife) ,*
*Okpri-Meila (daughter) & Muhamad Toshio (son)*

# Abstracts

Boronization as wall conditioning has been performed in many plasma devices, such as, TEXTOR at 150~350$^{\mathrm{o}}$C, DIII-D at 300$^{\mathrm{o}}$C, and JT-60U at 300$^{\mathrm{o}}$C, resulting in well reduced oxygen impurities and hydrogen recycling. In Large Helical Device (LHD), the boronization with glow discharge is also considered as the main technique to regulate wall surfaces. However, the temperature of the vacuum vessel is limited below 100$^{\mathrm{o}}$C. In this low temperature operation, the hydrogen content in the boron film is not sufficiently reduced. Therefore, a new technique to reduce the hydrogen content in boron film is desired by controlling glow discharge conditions during the boronization. To make clear the dependence of H content on discharge conditions and to establish techniques to evaluate the H content are main aims of this thesis.

The evaluation methods of hydrogen content were newly developed or modified. These are flash filament method (FF), residual gas analysis method (RGA) and ion beam analysis method (IBA). The principle and procedure of these methods are presented. In particular, the newly developed FF method gives us three advantages, that are, simple and quick operation, in-situ measurements, and absolute measurement.

In the newly constructed experimental facility named plasma processing teststand (PPT), in-situ analyses under films coating were carried out by using an oscillating quartz crystal for monitoring the thin film thickness, a movable Langmuir probe to measure the electron temperature and the electron density in the discharge, a quadrupole mass analyzer for monitoring gas evolution during the discharge and FF measurements, and a thermocouple and an infrared TV camera to monitor temperatures of films surface on the FF or on the cathode liner.

Hydrogenated amorphous boron films using decaborane or diborane gas and carbon films using methane gas were produced with well regulated conditions in plasma-assisted chemical vapor deposition P-CVD in DC glow discharges. Extensive and systematic researches to reduce the hydrogen content in low Z thin films were carried out at the room temperature condition in PPT by measuring 5 dependences on controllable parameters, which are discharge power, total gas pressure, pumping speed, gas flow rate and gases mixing ratio.

For the boron films from decaborane, it was found that the hydrogen content was successfully reduced with increasing the film growth rate. In cases of diborane and methane, although the discharge power dependence was in good agreement with decaborane, the pressure dependence did not agree with decaborane. For decaborane lower pressure results in the lower H content. However, for diborane and methane the higher growth rate of films leads lower H content as well as decaborane.

In order to make clear the influence of electrical potential of FF., boron films were produced on Al samples by floating or connecting to the cathode potential, and then, depth profiles of H were analyzed with the ERD of IBA technique. For this purpose, a new modified method using RBS was established to monitor the probing ion flux. Results showed that a high growth rate of film formation and the floating surface were effective in reducing hydrogen content in B films. From this results it is conjectured that energetic ions flux should be reduced but the radical one should be increased.

The results measured by using RGA and ion beam analysis ERD. showed a good agreement with FF.

Hydrogen reduction mechanisms to explain the experimental findings were discussed.

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# Chapter 1

# Introduction

Control of hydrogen particle recycling on plasma facing materials is considered to be one of key issues to improve plasma performance in Large Helical Device [1,2]. In LHD, on the other hand, low atomic number Z coating such as boronization of wall surfaces is considered as the main technique of wall conditioning, because the vacuum vessel is allowed to be baked at only the temperature below $100^{\circ}C$ [3,4]. In this low temperature range, however, the hydrogen content in such as amorphous hydrogenated boron films is not so sufficiently reduced [5] as performed in TEXTOR at $150 \sim 350^{\circ}C$ [6], DIII-D at $300^{\circ}C$ [7], and JT-60U at $300^{\circ}C$ [8], respectively, where, probably due to elevated wall temperatures, much suppression of hydrogen recycling resulted in clear improvement of the plasma parameters.

## 1.1 Objectives of Wall Conditioning in Fusion Devices

The wall conditioning in fusion devices is required to reduce the impurity concentration in the plasma and to reduce the H recycling on the wall to improve plasma parameters, especially the energy confinement. In other word, the main aim of wall conditioning is to produce surfaces which do not supply any kinds of particles as impurities into the plasma as far as possible, even under the heavy irradiation with energetic particles from the plasma. Here the particles are high Z impurities such as Fe, Ni, Cr, Ti, Mo and W, low Z impurities such as C, N and O, and recycling plasma fuels such as H, D, and/or He.

Undesirable effects of the impurities are the decrease of the fusion power density due to fuel dilution under the limitation of plasma pressure $\beta$ and enhanced energy losses through radiation processes. In case of bremsstrahlung the radiated power per impurity atom of the atomic number Z increases in proportion to $Z^2$. This was the main reason of the use of low Z coating to cover the high Z plasma facing components (PFC). However, often remains problems of uncontrollable fuel dilution due to excessive H recycling, that is, the recycling ratio R larger than unity, at the plasma start-up phase. This excessive hydrogen comes from the hydrogenated low Z film itself, because it is usually produced by using hydride gases. This excessive hydrogen in films is the target of this thesis.

## 1.2. Historical Background of Low Z Coating

Considerable improvement in plasma parameters has been obtained in the last decade with a better control of plasma surface interaction, particularly using low Z graphite or carbon fiber composite (CFC) materials as plasma facing components [9].

In 1984, the first test of the gettering with beryllium has significantly improved the properties of the tokamak plasmas in ISX-B [10], UNITOR [11], and recently in JET [12]. It has been shown that oxygen is effectively gettered by beryllium and consequently the concentration of oxygen and metallic impurities are significantly reduced. The low hydrogen recycling observed with Be compared with carbon, but beryllium has a problem due to low melting point.

Since Mid-November 1984, the first application of the carbonized liner and limiter in TEXTOR has opened up new fields of tokamak discharges [13]. Carbonization was curried out with plasma-assisted in-

situ chemical vapor deposition (P-CVD) of thin, amorphous, dense, hydrogenated carbon films (a-C:H) using $CH_4/H_2$ mixture gases on the entire inner surface of the liner. Carbonization led the tokamak plasmas to a significant improvement in comparison to the conditions achievable with RF-assisted glow discharge (RGD) cleaning with $H_2$ in TEXTOR. After the development of this procedure, carbonization has been applied in many fusion devices such as JET [14], ASDEX [15], JIPPT-IIU [16], and Heliotron-E [17]. Metal impurities were successfully reduced, whereas oxygen was not reduced probably due to recycling as CO [18]. Carbon coated layer is easily removed with the $H_2$ glow discharge. However, reversibility is also causally related to the erosion of a-C:H by hydrogen plasmas.

Veprek et al. suggested already in 1975/1976 to use boron or silicon carbide thin film coatings deposited onto the first wall by means of in-situ P-CVD [19]. Then in 1987, H.Toyoda et al. demonstrated the in-situ P-CVD of boron films from diborane $B_2H_6$ deposited on a toroidal vessel wall [5].

In March 1988, the first deposition of thin amorphous boron-carbide coating was performed in TEXTOR [20]. This technique is known as boronization by means of the RGD in a mixture of 10% $B_2H_6$, 10% $CH_4$ and 80 % He. Metal impurities in the core plasma became negligible, the carbon content was reduced, and there was a very strong reduction of oxygen impurities and H recycling. This result was considered as a great advantage of boronization compared to the carbonization. Since then boronization has been applied in many devices such as ASDEX, TFTR and TCA [20], and JT-60U [8].

In laboratory experiments on evaporated lithium coating, strong oxygen and hydrogen gettering effect was found [21]. However, understanding of hydrogen absorption on Li surfaces is still insufficient.

## 1.3. Boronization for Non Bakeable Devices

As described in previous section, boronization experiments in tokamak machines have shown that this wall conditioning procedure is a useful technique. In Japan, boronization has also been widely applied in plasma devices, such as JT-60U, Heliotron-E, CHS and JIPPT-IIU as briefly reviewed by A.Sagara [22]. In LHD, the boronization is also planed to be applied. The hydrogen content in deposited amorphous hydrogenated boron films was sufficiently reduced at elevated temperature in TEXTOR at $150 \sim 350^{\circ}C$ [6], DIII-D at $300^{\circ}C$ [7], and JT-60U at $300^{\circ}C$ [8], respectively, and the suppression of hydrogen recycling resulted in clear improvement of the plasma parameters. On the other hand, the boronization experiments in CHS have shown that hydrogen recycling was not successfully reduced at room temperature [23]. It has been found that the hydrogen recycling was significantly reduced only when the wall temperature was elevated over $200^{\circ}C$ [6-7]. But, not all devices can be allowed to elevate the wall temperature over $200^{\circ}C$. Therefore, another technique beside baking is required to reduce the excessive hydrogen content in coated films..

It is well known that H recycling depends on boronization methods and/or conditions [22]. Then, the purpose of this thesis is to systematically investigate the dependence of hydrogen concentration on discharge conditions and to optimize the boronization condition for general use, especially for LHD, the vacuum vessel of which is limited below $100^{\circ}C$.

## 1.4 Out Line of Thesis

This thesis consists of six chapters. In chapter 2, evaluation methods of hydrogen content developed for this study are formulated. The experimental set-up and procedures are described in chapter 3. The experimental results and discussion are presented in chapter 4. The model and the common results obtained with the experiment are summarized in chapter 5. Finally, the thesis is concluded in chapter 6.

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# Chapter 2

# Development on Evaluation Methods
of Hydrogen Content

In order to prevent any contaminations of coated films, hydrogen analysis should be carried out using in-situ techniques. Therefore, one of main parts in this study is the development of new methods for in-situ determining the hydrogen content in coated films.

## 2.1 Conventional Techniques

The conventional techniques for detecting hydrogen in solids and measuring its concentration quantitatively are not very plentiful. The hydrogen content of tokamak walls have been measured using collected samples by ex-situ analysis methods like infrared absorption spectroscopy (IR) [1], secondary ion mass spectroscopy (SIMS) [2], elastic recoil detection (ERD) [3], resonance nuclear reaction method (NRA) [4,5], and thermal desorption spectroscopy (TDS). It can be expected that air exposure of coated samples could lead to discrepancies between the results of ex-situ and in-situ analysis due to the possibility of water vapor adsorption. IR technique can be used only for the detection of bonded hydrogen atoms, and quantification requires a calibration sample of known H content in the same bonds to determine oscillator strength. The mass of H atom is too light to back scatter the any ions in Rutherford backscattering (RBS). H can be observed with SIMS, but, since the ionization probability is strongly influenced by the surface composition itself, accuracy is still poor for absolute measurements of H. Therefore

development of new methods which allow in-situ measurements is desired.

## 2.2. New and Modified Techniques [6-8]

Two methods for determining the hydrogen content in low Z thin films have been developed in this work, that are, the flash filament (FF) method and the residual gas analysis (RGA) method. The FF method was first developed [6], and this new method gives us three merits, that are, simple and quick operation, in-situ measurement and absolute measurement. The modified ex-situ ion beam analysis using 1.5 MeV $He^+$ was also used for hydrogen depth profiling.

### a) Flash Filament Method (FFM)

The principle of flash filament technique for measuring hydrogen concentration is described as follows : a thin tungsten wire named flash filament is inserted in the chamber and coated together with the cathode during a discharge. Then, the filament is flashed to 1300K with monitoring desorbed hydrogen with RGA. The amount of H atoms in the film is estimated from the desorbed hydrogen amount $\Gamma_H$ (atoms) with an assumption that all hydrogen atoms in the deposited films are desorbed by the heating. The atomic ratio H/B of hydrogen to boron in a coated film is calculated as the following equation,

$$\frac{\Gamma_H}{d_f} \propto \frac{(\Gamma_H / A_f)}{(\rho_B \, d_f / M_B)} = \frac{H}{B} \quad , \qquad (2\text{-}1)$$

$A_f$ : the flash filament area ( $cm^2$ )

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$\rho_B$ : the boron density ( g/ cm$^3$ )

$M_B$ : the atomic weight ( g/atom ) of B

The film thickness $d_f$(cm) is measured with a quartz oscillator under the given value of $\rho_B$, which is supposed to be 1.5 g/cm$^3$ [9,10] in this study. The oscillator essentially measures the surface mass density $\rho_B d_f$ deposited on the oscillator. So the accuracy of $\rho_B$ is not important in eq.2-1. The H/B ratio is proportional to $\Gamma_H/d_f$ according to eq.2-1, so this value is used as a measure of H concentration, because the evaluation of $A_f$ is not impossible but not easy. The detail of experimental procedures will be shown in the next chapter with description of experimental apparatus.

## b) Ion Beam Analysis (IBA)

The majority of the primary incident ions are moving forward and eventually stop inside sample substrate. Only a very small portion of the ion beam is backscattered and detected by RBS analysis. The number of scattered particles from the substrate surface, namely the edge intensity in the RBS spectrum, $Y_R$ (counts/ch) can be written as,

$$Y_R = F \cdot N_S \cdot \frac{\sigma_R(E_1)}{\varepsilon_R(E_1)} \cdot \Omega_R \cdot \Delta E_R \quad , \qquad (2\text{-}2)$$

where,

F is the total number of incident particles (atoms),

Ns is the atomic density of the substrate (atoms/cm$^3$),

$\sigma(E_1)$ is the differential elastic scattering cross section (cm$^2$/str.)

as a function of the primary ion energy Ex at depth x, here x=1,

$\varepsilon(E1)$ is the stopping power (eV/cm),

$\Omega$ is the solid angle of detector (str.)

$\Delta E$ is the energy width per detection channel (eV/ch)

Then, the total number F of incident particles is obtained from eq.2-2.

The principle of the ERD is similar to that of RBS. In both cases an elastic scattering event is essential. However, instead of analyzing the primary ions scattered from target atoms, in case of ERD the hydrogen atoms recoiled with primary ions are detected. Then, after the same manner as the case of RBS, the H concentration $N_H(x)$ ( atoms/cm$^3$) from ERD spectrum is given as a function of depth x by,

$$N_H = \frac{Y_H \cdot \varepsilon_E(Ex)}{F \cdot \sigma_E(Ex) \cdot \Omega_E \cdot \Delta E_E}, \qquad (2\text{-}3)$$

where, $Y_H$ is the number of counts of hydrogen atoms detected (counts/ch).

In order to obtaine the depth profile from ERD spectrum, the stopping powers of $^4$He and $^1$H have to known. In this work, the value of Ziegler [11,12] have been taken from tables and the scattering crossection have been computed from Rutherford formula.

## 2.3 Residual Gas Analysis (RGA)

The hydrogen concentration is also measured from residual gas analysis during the discharge as a complementary method. Hydrogen atoms are injected to the chamber in the form of $B_mH_n$ or $C_mH_n$. Most of them are dissociated and deposited on the wall. However some part of

injected molecules are directly pumped out. Hydrogen atoms are also pumped in the form of $H_2$, which are produced in the plasma or surface recombination on the film. The hydrogen concentration in the film is estimated from the difference between injected and pumped H atoms and expressed as follows [8],

$$\Phi_H = \frac{K(n\beta Q_{in} - 2S\Delta P)}{A_c} \quad , \qquad (2\text{-}4)$$

$\Phi_H$ : the hydrogen flux trapped in the film (H atoms/cm$^2$ s)

n : the number of hydrogen atoms per sample gas molecule ( n = 6 for diborane, n = 4 for methane, and n = 14 for decaborane )

$\beta$ : the averaged dissociation ratio of the molecule; the molecules not dissociated are supposed to be pumped out of the system.

$Q_{in}$ : the input flow rate (Torr l/s) of the sample gas containing H atoms

S : the pumping speed (l/s) for $H_2$ gas

$\Delta P$ : the $H_2$ partial pressure difference from the initial value before gas injection (Torr)

$A_c$ : the total liner area (cm$^2$), where $A_c$ = 1080 cm$^2$ in this study.

K : the constant of 3.54 x10$^{19}$ atoms/ Torr litre

The deposition flux of coating atoms $\Phi_B$ is estimated from the growth rate $G_f$,

$$\Phi_B = (\rho_B / M_B) G_f \quad , \qquad (2\text{-}5)$$

$\Phi_B$: the boron flux on the film ( B atoms/cm$^2$ s)

$G_f$ : the growth rate of film (cm/s)

Then the H/B ratio, for instance, is obtained using the following equation,

$$\frac{H}{B} = \frac{\Phi_H}{\Phi_B} = \frac{\Phi_H}{(\rho_B G_f / M_B)} \quad , \qquad (2\text{-}6)$$

Deposition ratio $R_d$ of B or C is also estimated with the equation,

$$R_d = \frac{(\rho_B G_f / M_B)}{(mKQ_{in})} \quad , \qquad (2\text{-}7)$$

where m is the number of B or C atoms per sample gas molecules (m = 2 and 1 for $B_2H_6$ and $CH_4$, respectively).

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# Chapter 3

# Experimental Set-up and Conditions [1,2]

In this chapter, experimental apparatus and procedures are described. The B:H films or the C:H films are prepared by the plasma assisted chemical vapor deposition (P-CVD) in DC glow. As measuring tools, the Langmuir probe, RGA, thickness monitor, flash filament, infrared TV camera, thermocouple, ionization gauge, and a diaphragm gauge have been used.

## 3.1  Experimental Apparatus

### a) Plasma Processing Teststand (PPT)

A newly constructed plasma processing teststand (PPT) apparatus is shown schematically in Fig.1. The vacuum vessel is a stainless steel cylinder of 152 mm in diameter and 400 mm in length. It has a total volume of 6.6 liter. The PPT system is equipped with safely gas handling system, gas introduction system controlled by three separate mass flow controllers and turbomolecular pump unit with a nominal pumping speed of 200 l/s. The chamber is pumped with the effective pumping speed, $S_{eff}$, of 25 l/s. A precision valve for pumping out of the system is applied to control the pumping speed during discharge experiments.

The cathode (liner) crossection is square, which consists of 4 pieces of stainless steel sheet with size 300 mm x 90 mm x 1 mm bundled into a cylindrical vessel. The inner surface of the liner is of 1080 cm$^2$. The anode is a stainless steel rod of 2 mm in diameter and 300 mm in length
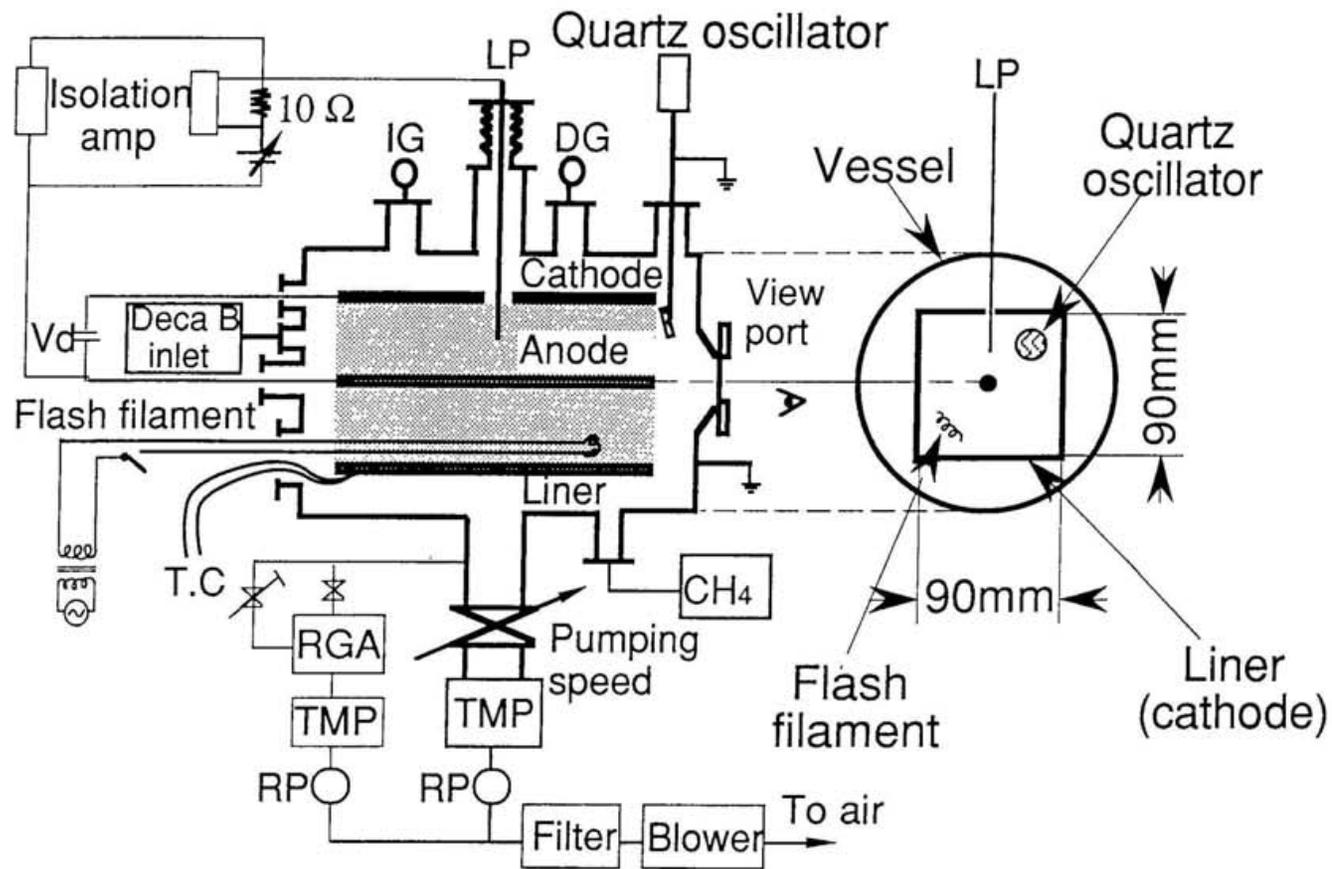
Fig. 1 Schematic diagram of PPT apparatus.

placed at the center of the liner crossection. The distance between the anode and the liner was 4.5 cm. Both the cathode and the anode were electrically isolated from the ground to make the discharge at only the inside of the cathode liner.

### b) Thickness Monitor

The thickness monitor is placed at one end of the liner as shown in Fig.1. Thin film thickness measurements during deposition are generally accomplished by the use of oscillating quartz crystal known as a " thickness monitor ", which is simply a piezoelectric quartz AT-cut ~ 5 MHz. Early investigations on quartz crystal resonators by Sauerbrey [3] and Lostis [4] indicated that, for small mass charges on a crystal, the decrease in a thickness shear vibration mode frequency of the crystal is linearly proportional to deposited mass. The quartz crystal monitor gives an absolute reading of film thickness by giving the weight density of the film [5], accuracy of which is not important as noted in 2.2.a.

In order to confirm measurements, the coated boron films on collector samples are additionally determined by an independent reference method. Measurements are performed by using ion beam analysis as discussed below.

Crystal temperature control is important. If the crystal heats up during a deposition measurement due to radiation or others from the discharge, frequency will increase and appear as a decrease in thickness. If the radiation is coming from the discharge, transient error due to quartz temperature rise will occur at the start of deposition, and again due to cooling down at terminating discharge as typically shown in Fig.2. These transient can be recognized most easily by recording thickness versus time.

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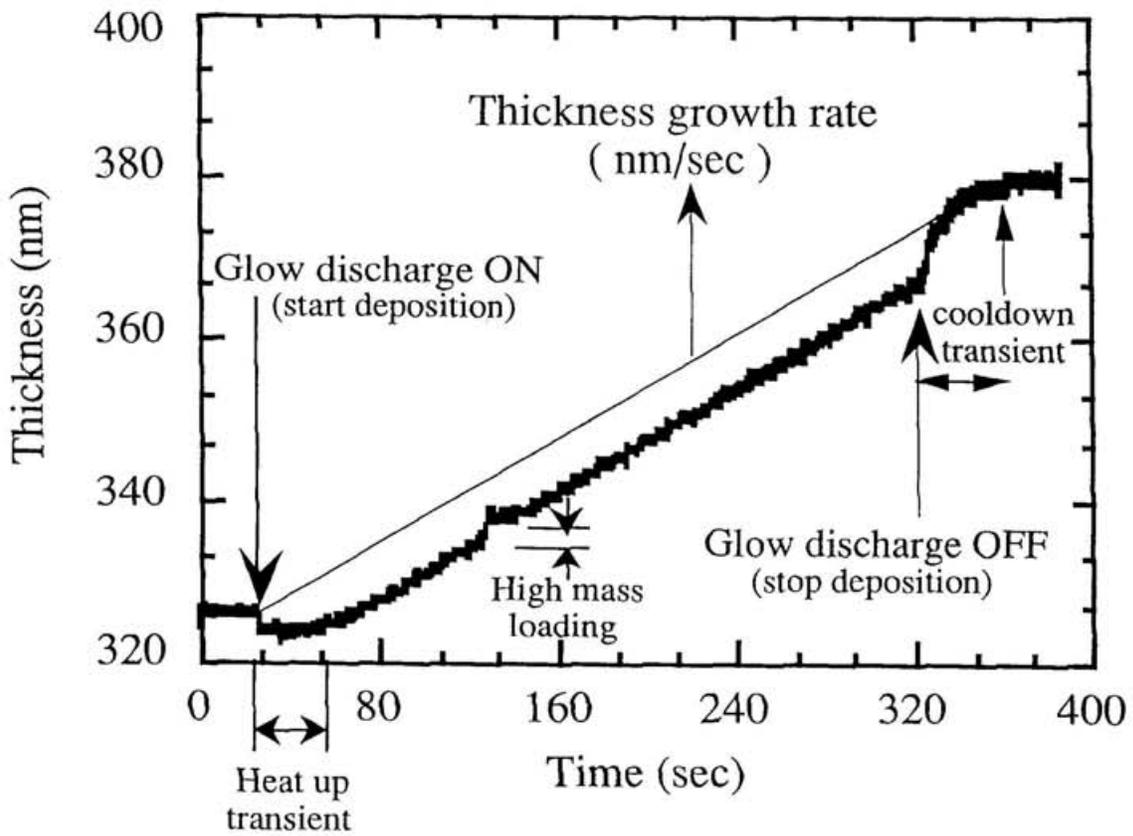
Fig. 2. Quartz monitor film thickness film versus
time ( typical experimental results from
boronization with decaborane )

The actual growth rate is the slope in the linear region as shown in Fig. 2.

### c) Langmuir Probe (LP)

A tungsten single Langmuir probe of 0.3 mm in diameter and 3 mm in length was placed in the liner for monitoring the plasma parameter during the discharge. The probe position can be changed in vertical direction from the anode to the cathode, and was mainly set at 30 mm away from the centered anode. The Langmuir probe surface was cleaned by heating up to $1000^{o}C$ with electron bombardment in a pure helium glow discharge prior to every boronization cycle, by operating the probe at highly positive potentials of about 70 V. Then, after initiation of boronization discharge, we measured several I-V characteristic curves, which took acquisition time of 5 sec each. The measured I-V characteristic was stored in a Macintosh computer through AD converter. By fitting data to this curve, the plasma density and electron temperature were derived. The total error for $T_e$ and $n_e$ of our experiments was estimated to be about 5 %.

### d) Flash Filament Apparatus

The schematic of FF method apparatus is shown in figure 3. A tungsten wire of 0.2 mm in diameter and 40 mm in length was inserted between the anode and liner as the flash-filament. It was set at electrically floating potential to avoid heating up due to discharge current. The distance between the flash filament and the anode was set to be quite similar to that between quartz oscillator and anode, to minimize the effect of plasma inhomogenity.
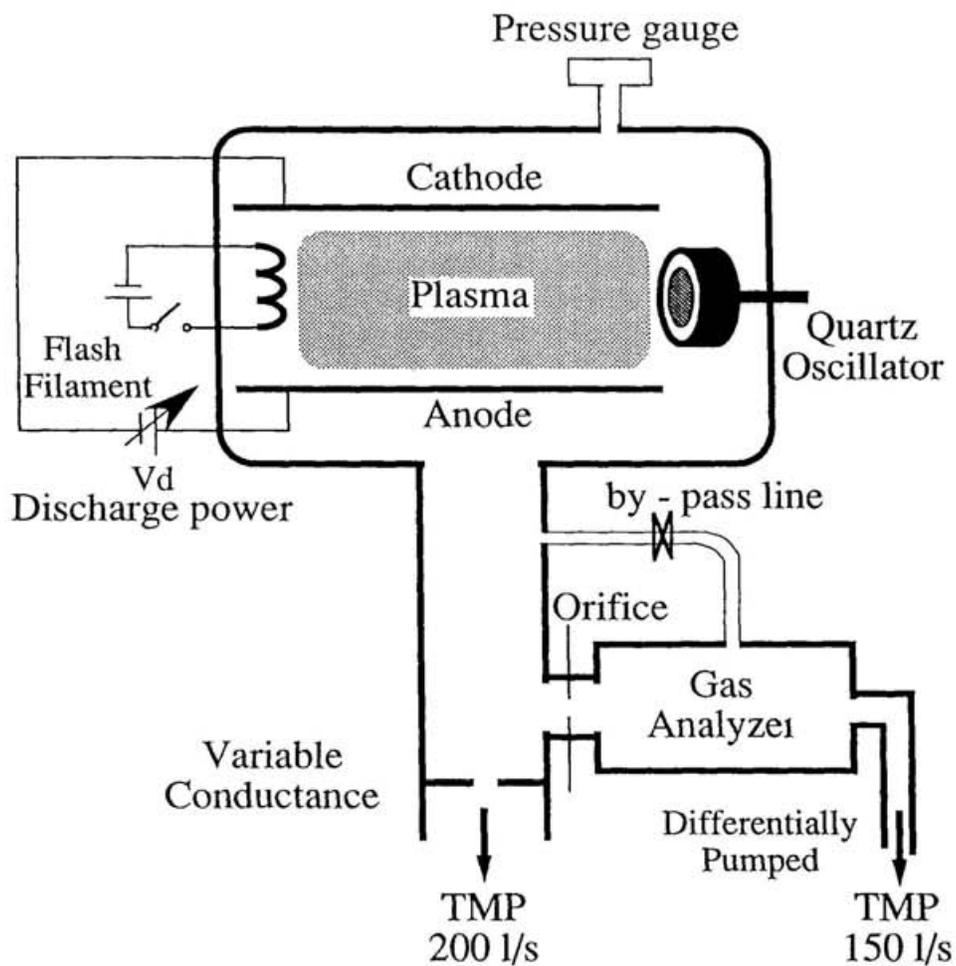
Fig. 3. Apparatus of Flash Filament Desorption Method

After each boronization run, during which the filament was also coated, the system pumping speed was set to 4 l/s with He by adjusting precision valve. Then the filament was flashed with monitoring desorbed $H_2$ with RGA calibrated by ionization gauge. The FF was operated at power input of 22.2 Watt, voltage of 6 V and current of 3.7 A. It should be noted that the filament was flashed to $1500^{\circ}C$ for several sec in vacuum prior to each boronization run to remove hydrogen and other contamination. This procedure successively removed any surface contaminants and thus, highly reproducible hydrogen spectra can be obtained.

In Fig. 4, a typical desorption spectra for hydrogen from boron coated film produced with different pressure are shown. From the curve, the desorbed amount of H was estimated as following.

### e) Residual Gas Analyzer (RGA)

For a gas analysis during the discharge, a residual gas analyzer was connected to the discharge chamber through a small orifice and differentially pumped to keep the total pressure in the RGA chamber below $10^{-5}$ Torr. A schematic diagram of the experimental arrangement for partial pressure analysis is also shown in figure 3. The residual gas analyzer was also used for flash filament method during which the orifice was by-passed to increase sensitivity of the RGA. Figures 5 and 6 show typical time evolutions of partial pressures taken with residual gas analyzer (RGA) before and during discharge for diborane and methane.

In order to estimate the hydrogen partial pressure from the RGA signal, a calibration was performed in the following procedure. At each given flow rate of hydrogen gas from 1 to 10 sccm, the intensity of hydrogen signal was measured by RGA, and the pressure of hydrogen
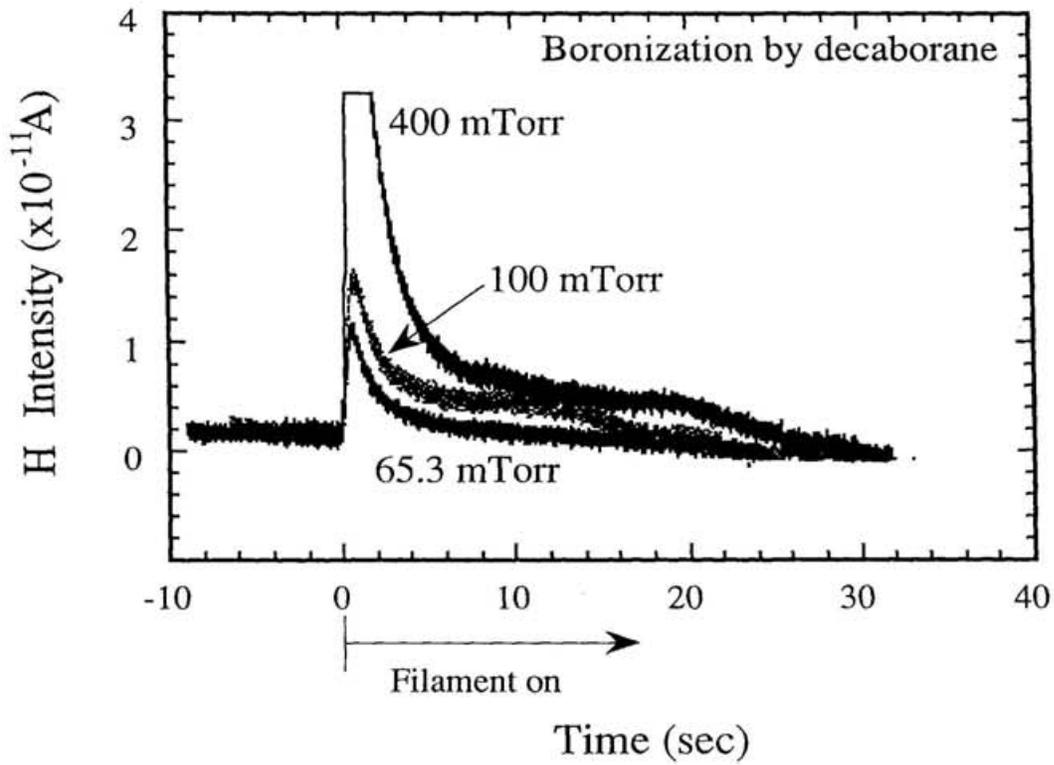
Fig. 4. Typical Flash Filament spectra of hydrogen from boron coated film under total pressure dependence taken with RGA
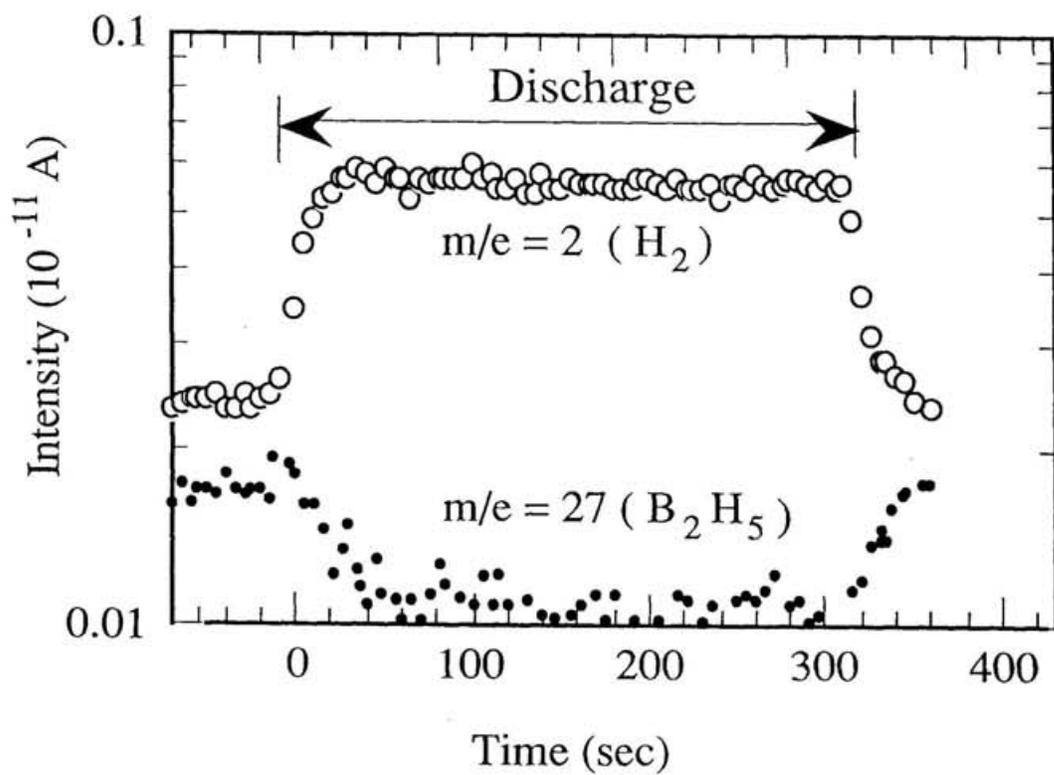
Fig. 5. Time evolutions of the two representative
of partial pressures taken with RGA
for discharges with $B_2H_6$ (5%) + He
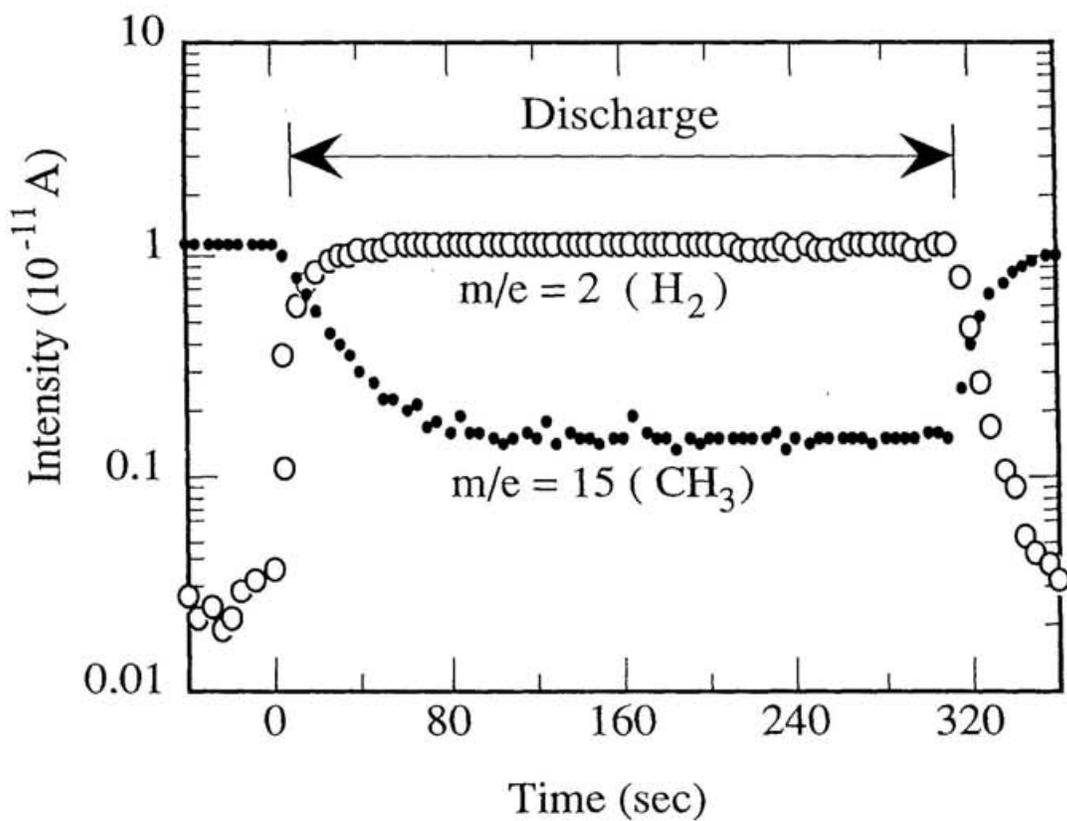
Fig. 6. Time evolutions of the two representative
of partial pressures taken with RGA
for discharges with CH4 (100 %).

were measured by diaphragm gauge. Then, the calibration curve was plotted between the intensity in Ampere and partial pressure in Torr as shown in Fig. 7.

### f) Temperature Monitor

Thermocouple pairs of chromel and alumel type and infrared TV camera were used to monitor temperature. The thermocouple was attached strongly to the liner, to have a good thermal contact. The infrared TV camera was operated for monitoring surface temperatures during growing films. A typical temperature profile in the coating chamber during film growth is shown in Fig.8. In general, the liner temperature during discharge was kept below $90^{\circ}C$

### g) Hydrogen Elastic Recoil (ERD) Arrangement [6-7]

After each boronization and FF measurement, the coated samples were taken out from PPT chamber to atmosphere for the following ion beam analysis. Non-destructive ion beam analysis using 1.5 MeV He$^+$ ions was performed to measure the film thickness with RBS and to measure the hydrogen depth profile with ERD. 1.5 MeV MeV He$^+$ ions were produced with the AN-2000 accelerator Van de Graaff belongs of the Nagoya university. Two solid state detector for ERD and RBS measurements were installed in the analysis chamber. Experimental setup is schematically shown as in Fig. 9 and is described in detail in [7]. Briefly, the incidence angle of the ion beam was $10^{\circ}$ from the sample surface. A solid state detector for ERD was placed at the recoiling angle of $20^{\circ}$ from the probe beam, with a slit and a mylar filter of 6 μm thick to cut the scattered He ions. In order to monitor the probing ion fluence, the RBS detector was set at $150^{\circ}$ from the probe beam. The absolute efficiency of the ERD measurement system was calibrated by using a
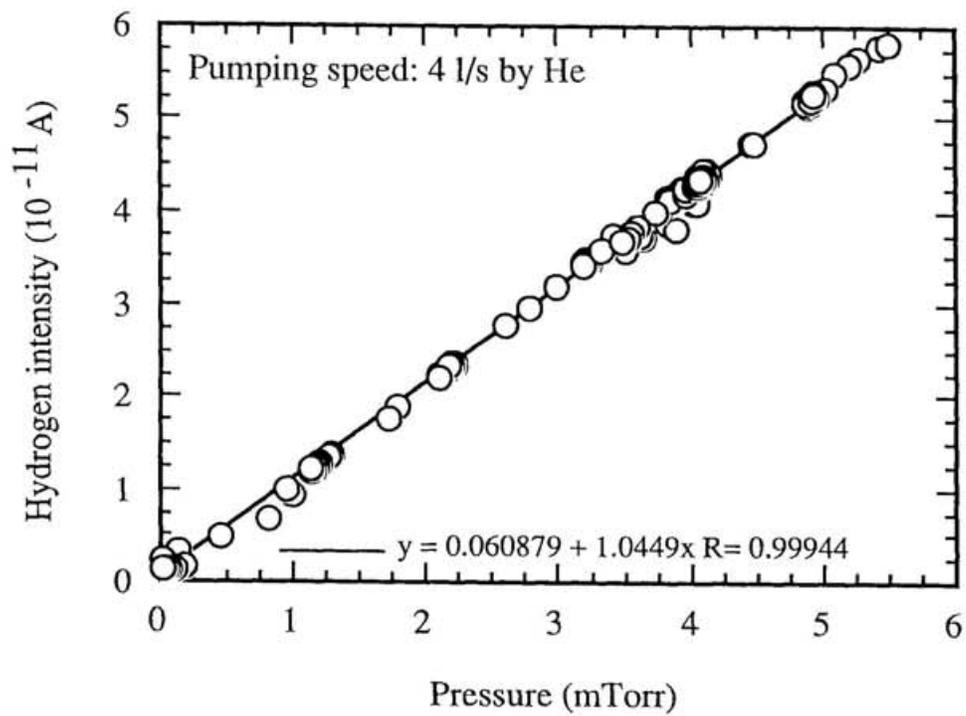
Fig. 7. Calibration curve between H intensity (nA)
and H partial pressure (Torr).
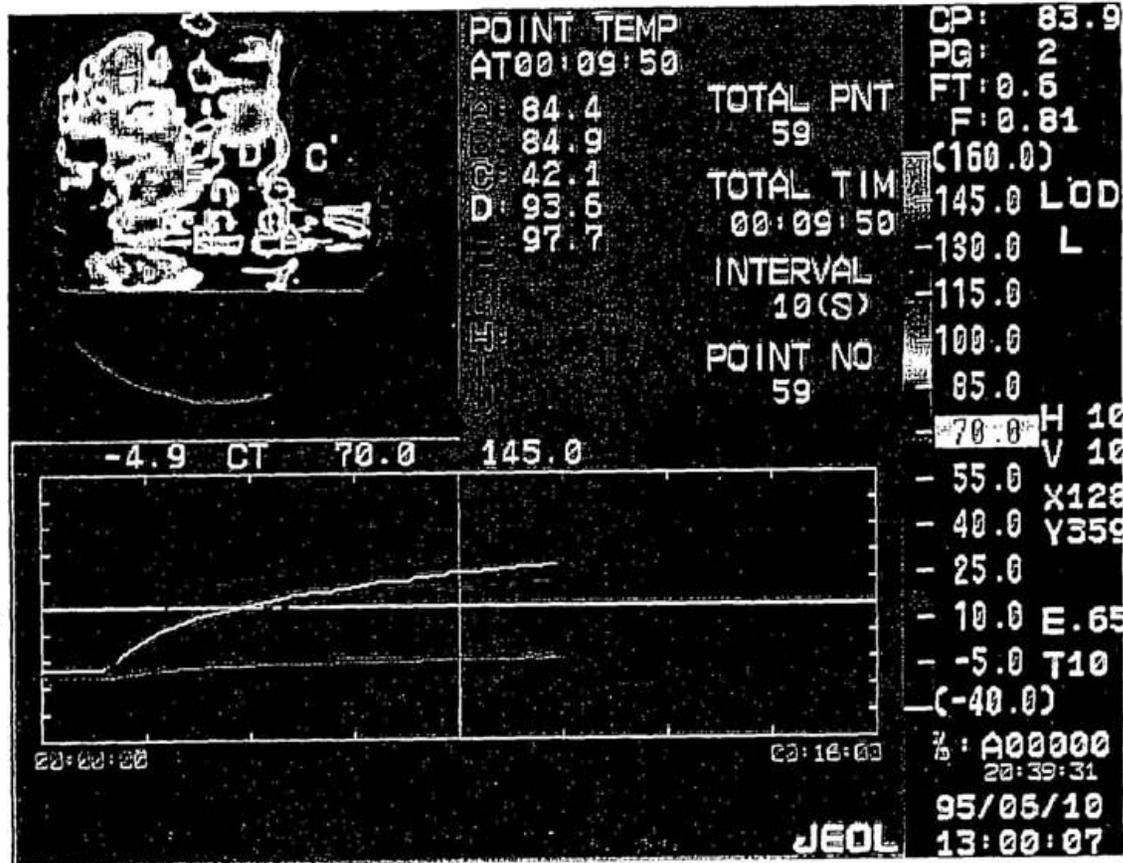
Fig. 8. Temperature profile measure with IR TV camera
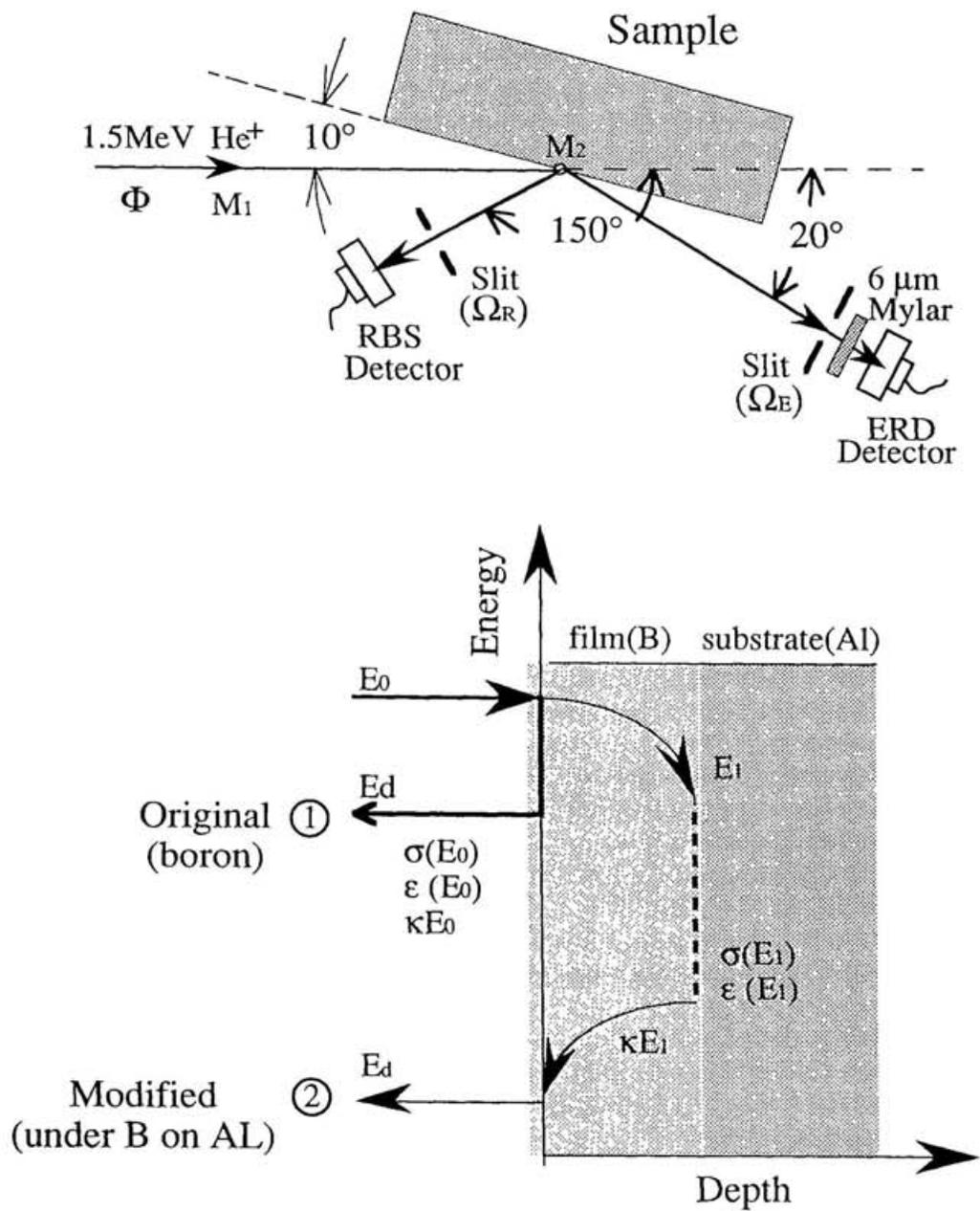
Fig. 9. Schematic illustration of the experimental arrangement
for profilling H in low Z thin films

vanadium hydride ($V_2H$) standard sample. Here, the mass density of the B coated film was assumed to be 1.5 g/cm$^3$ [8,9]. The base pressure in the analysis chamber during the experiments was about 10$^{-8}$ Torr. A personal computer system was used for data acquisition and analysis, and final output was plotted in the form of particle yield vs channel number.

## 3.2 Discharge Procedure and Conditions

The gases used in the experiments are decaborane, pure methane, diborane diluted in He, and pure helium and pure hydrogen. The experimental procedures using methane or diborane were same as decaborane as shown in Fig. 10.

### 3.2.1 Boronization with Decaborane

In case of decaborane, about 5 gram decaborane solid was placed in a tantalum cup placed in a glass crucible covered with a tantalum heater in a stainless steel mini-chamber. The decaborane was heated up to 200$^o$C with a feed-back control system through a thermocouple directly spot welded to the cup. The base pressure in the range of 10$^{-7}$ Torr was formed by a turbomolecular vacuum pump. Then, decaborane and helium gas were introduced into the vacuum vessel separately through individual mass flow controllers. The vacuum condition was monitored by an ionization gauge, a diaphragm gauge, and a quadrupole mass analyzer (RGA). The whole of decaborane inlet system including the mass flow controller is warmed up and kept at 120$^o$C. Decaborane vapor was injected straight into the discharge area as shown in Fig. 1.

In the PPT system the controllable ranges of the system pumping speed are as follows: pumping speed $S_0 < 12.7$ l/s calibrated with helium, He flow rate $Q_{He} < 50$ sccm, $B_{10}H_{14}$ flow rate $Q_B < 2$ sccm, He pressure

Preparation $\dashrightarrow$ Evacuation base pressure $10^{-7}$ Torr

Calibration pumping speed $\dashrightarrow$ He gas 4 l/s or 2 l/s

He glow , Electron bombardment ~ $1000^0$ C for LP

Cleaning for LP, flash filament, and Chamber

Boron or Carbon films produced by DC glow dicharge $\dashrightarrow$ Monitored, RGA (Partial Pressure) Langmuir probe (Te, ne), Quartz oscillator (thickness)

Ion Beam Analysis
- RBS
- ERD

Boron / Carbon film flashed to desorb Hydrogen $\dashrightarrow$ Flash desorption filament (H Content) RGA (Hydrogen spectra)

Fig. 10. General scheme of experimental procedure for controlling hydrogen conten in boron film.

P > 50 mTorr to maintain stable discharge, and discharge power $I_dV_d <$ 400 W at stable state. Within these parameter ranges the standard discharge condition was arranged at $S_O = 4$ l/s for He, $B_{10}H_{14}$ mixing ratio $R_B = P_B(B_{10}H_{14})/P_d(B_{10}H_{14}+He) = 6$ % with $Q_{He} = 29.1$ sccm and $Q_B = 0.6$ sccm, $P_d(B_{10}H_{14}+He) = 100$ mTorr, and $I_dV_d = 100$ W with $V_d$ ~300 V. Around this standard condition, each parameter was varied with measuring the hydrogen concentration, B film growth rate, electron temperature $T_e$, and electron density $n_e$. Here, it should be noted that a pressure P and a flow rate Q are not able to vary independently, because $Q = S_OP$ with a pumping speed $S_O$. In this work, therefore, the total 5 combinations in parameter dependences of boronization were first systematically investigated except for temperature dependence. That is, discharge power dependence under standard condition, total pressure dependence with constant flow rate, pumping speed dependence with constant pressure, flow rate dependence with constant pumping speed, mixing ratio dependence under standard condition, respectively.

### 3.2.2 Carbonization with Methane and Boronization with Diborane

In cases of methane and diborane, before starting boronization or carbonization, the stainless-steel liner as the cathode was changed to new one, and cleaned by helium glow discharge for 20 minutes. After evacuated below $10^{-6}$ Torr, sample gases were introduced into the chamber with typical flow rates in the range of 5 to 50 sccm and the pressure in the range of 60 to 400 mTorr by adjusting pumping speed. Coated films were prepared under DC glow discharge with the input power of 80 to 300 W at the voltage between 300 to 500 V. During the discharge the operation parameters were essentially fixed at constant conditions, and the plasma was analyzed using a Langmuir probe, before

fully contaminated the probe surface under coating. All of coating films were prepared in 5 minutes at room temperature. The film thickness was in the range between 4 to 100 nm in each discharge for 5 min. After quick evacuation of sample gases, the flash filament method (FFM) described below was applied. Lastly, the Langmuir probe was cleaned by heating up with electron saturation current in helium glow for 5 minutes. This one set of procedure was repeated systematically by changing experimental parameters. For diborane gas mixtures ($B_2H_6$+He) or pure methane ($CH_4$), discharge power dependence and total pressure dependence were systematically investigated. H concentration was obtained as functions of two of these parameters of discharge conditions.

### 3.2.3 Effect of Floating and Cathode Potential Samples

As is mentioned previously, the FF was set at electrically floating potential to avoid heating up due to discharge current. The potential difference between the plasma and the FF will be the floating potential, $V_f$, which is given approximately by Chen [10],

$$V_f = (kT_e/2e)\ln(2\Pi m/M_i) \quad , \tag{3-1}$$

where, the symbol $T_e$ is the electron temperature, $M_i$ and m are the ion and electron mass, respectively, and k is the Boltzman constant. $V_f$ is typically 10 V for the glow discharge plasmas in which $T_e \sim 3$ to 5 eV. This means that surfaces at floating potential are exposed to ion bombardment of around 10 eV. On the other hand, for the cathode potential sample, the ions energy is determined by the discharge voltage between the anode and the cathode, and the bombarding energy becomes of the order of a few hundred volts.
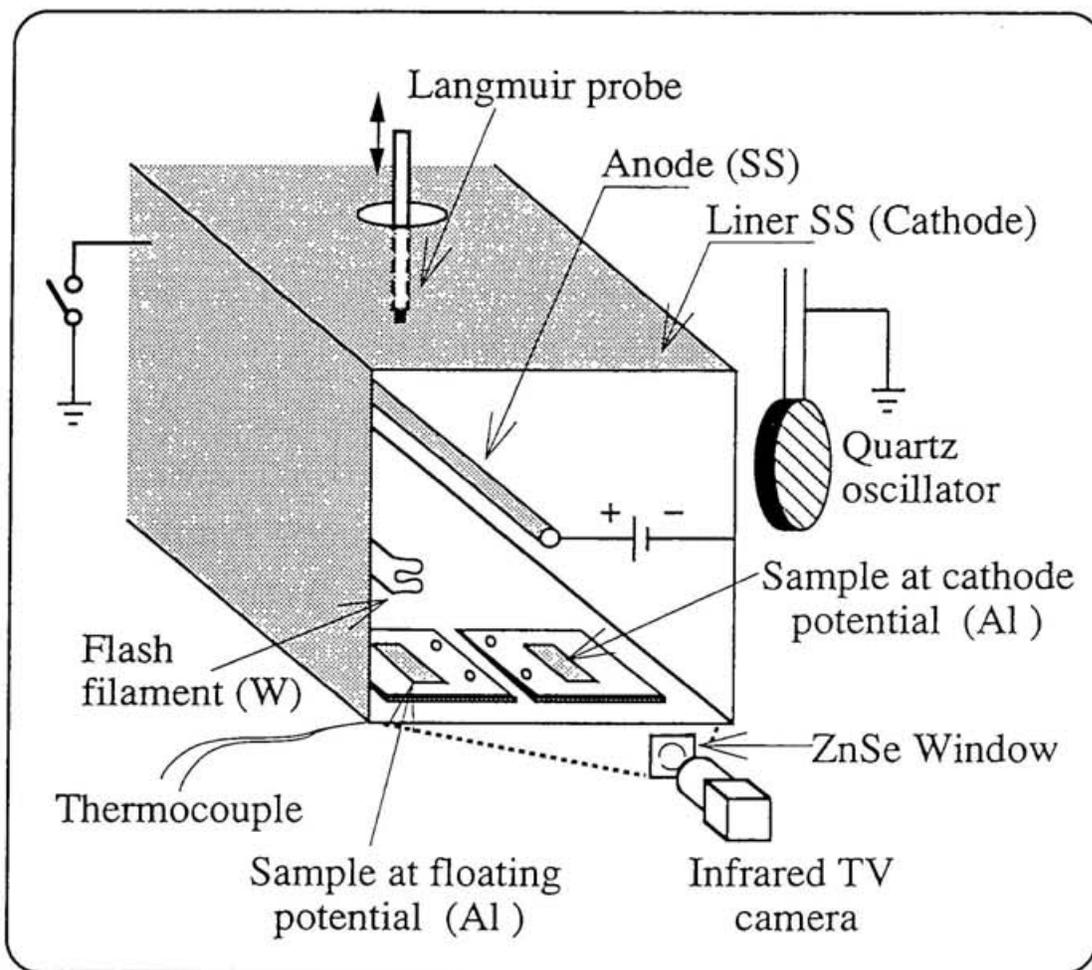
Fig. 11. The schematic illustration of the PPT device
with showing locations of the Al samples.

In order to make clear influence of electrical potential of FF, boron films were prepared on floating and cathode potential samples, and depth profiles of H were analyzed with ERD technique. For this purpose, a schematic diagram of the experimental set-up is shown in Fig. 11. A mixture gas of 5% $B_2H_6$ + He was introduced up to the total pressure in the range of 60 to 200 mTorr with the pumping speed of 4 l/s for He. Boron films were prepared under DC glow discharge with the input power range of 80 W (300 V, 0.27 A) to 300 W (600 V, 0.5 A). By considering the maximum sampling depth and depth resolution of ERD described before [7], the optimum thickness of boron film was selected at about 100 nm. The films thickness was tentatively monitored with a quartz oscillator. After each boronization and FF measurement, the coated samples were taken out to atmosphere for the following ion beam analysis.

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# Chapter 4

# Experimental Results and Discussion

## 4.1. Boron Coating with Decaborane ($B_{10}H_{14}$)

The concentration of hydrogen in the films has been determined by flash filament method. Figure's 12 (a),(b) to 16 (a),(b) show the parameter dependencies of boronization characteristics measured in this work. It can be observed in common in each figure (a) that the hydrogen concentration is relatively low when the film growth rate is high [1]. This result can be explained that, if the sticking probability of hydrogen dissociated from $B_{10}H_{14}$ molecules is much lower than boron contained gas species, the opportunity of hydrogen incorporation into film layer is low as the film growth rate is high. Thus, the hydrogen content in the film deposited with high growth rate is low.

*Discharge power dependence under standard condition*

In Fig.12 the hydrogen content decreases as discharge power increases. In this case it is simply presumed that active species such as radicals and ions might increase due to increase of the input power for discharge. Then the film formation rate is accelerated, resulting in suppression of hydrogen content in boron film layer. At high power the liner temperature are in the range of $80 \sim 85^{\circ}C$.

*Mixing ratio dependence under standard condition*

In Fig.13 (a) and (b), higher mixing ratio of $B_{10}H_{14}$ gas results in lowering the hydrogen concentration with increase of the film growth rate. When the mixing ratio is high, the relative amount of the reactive

**(a)** Total Pressure : 100 mTorr
$B_{10}H_{14}$ mixing ratio : 6 %
He flow rate : 29 sccm
$B_{10}H_{14}$ flow rate : 0.6 sccm
Pumping speed : 4 l/sec

Growth rate
(nm/min)

H concentration
(a.u)

**(b)**

0.045

-5  0  +5

$n_e$ ($\times 10^{11}$ cm$^{-3}$)

$T_e$(eV)

Discharge power (W)
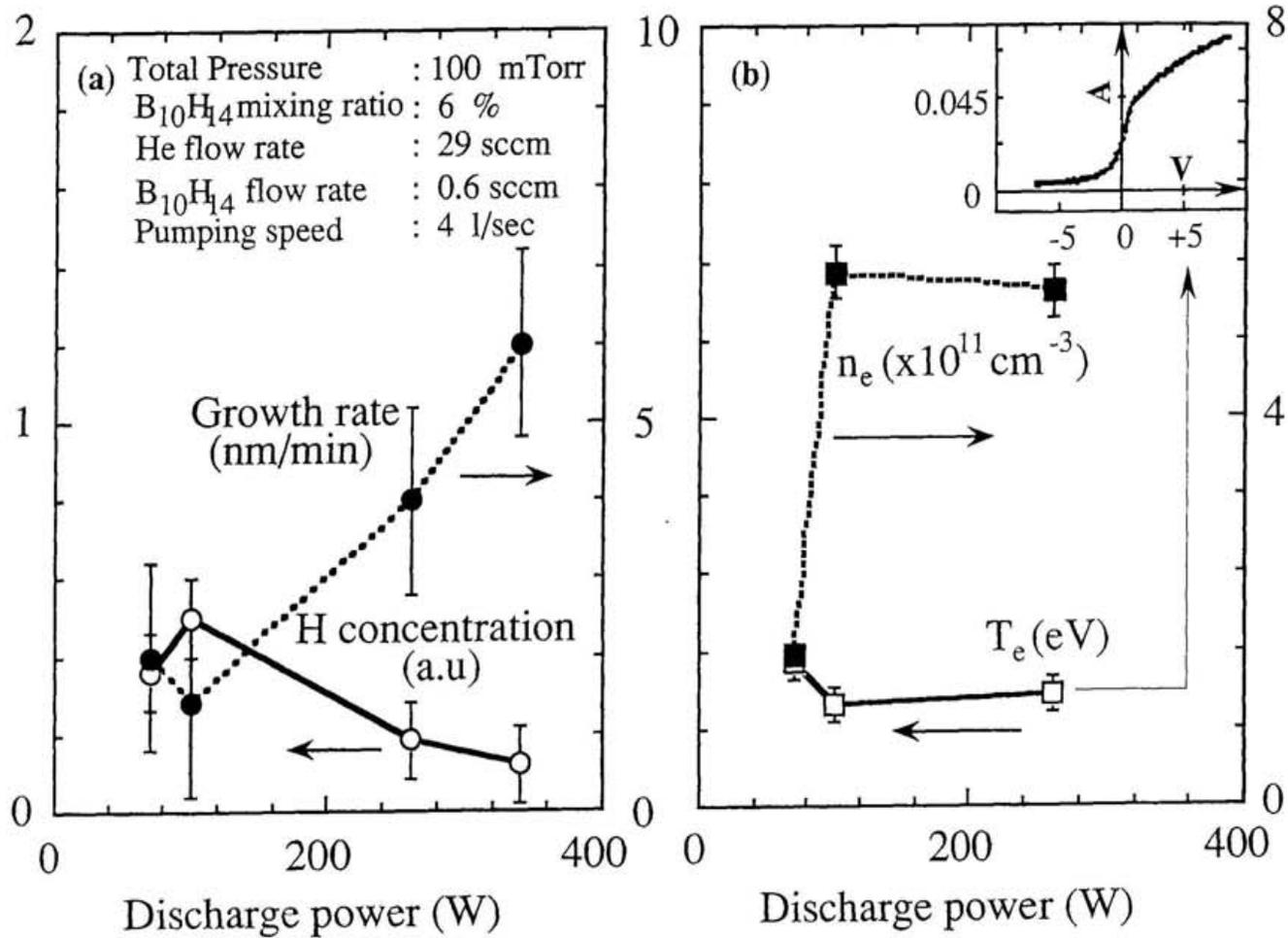
Discharge power (W)

Fig. 12. The discharge power IdVd dependence under standar condition of
(a) the hydrogen content and the film growth rate, and
(b) the electron temperature and density.
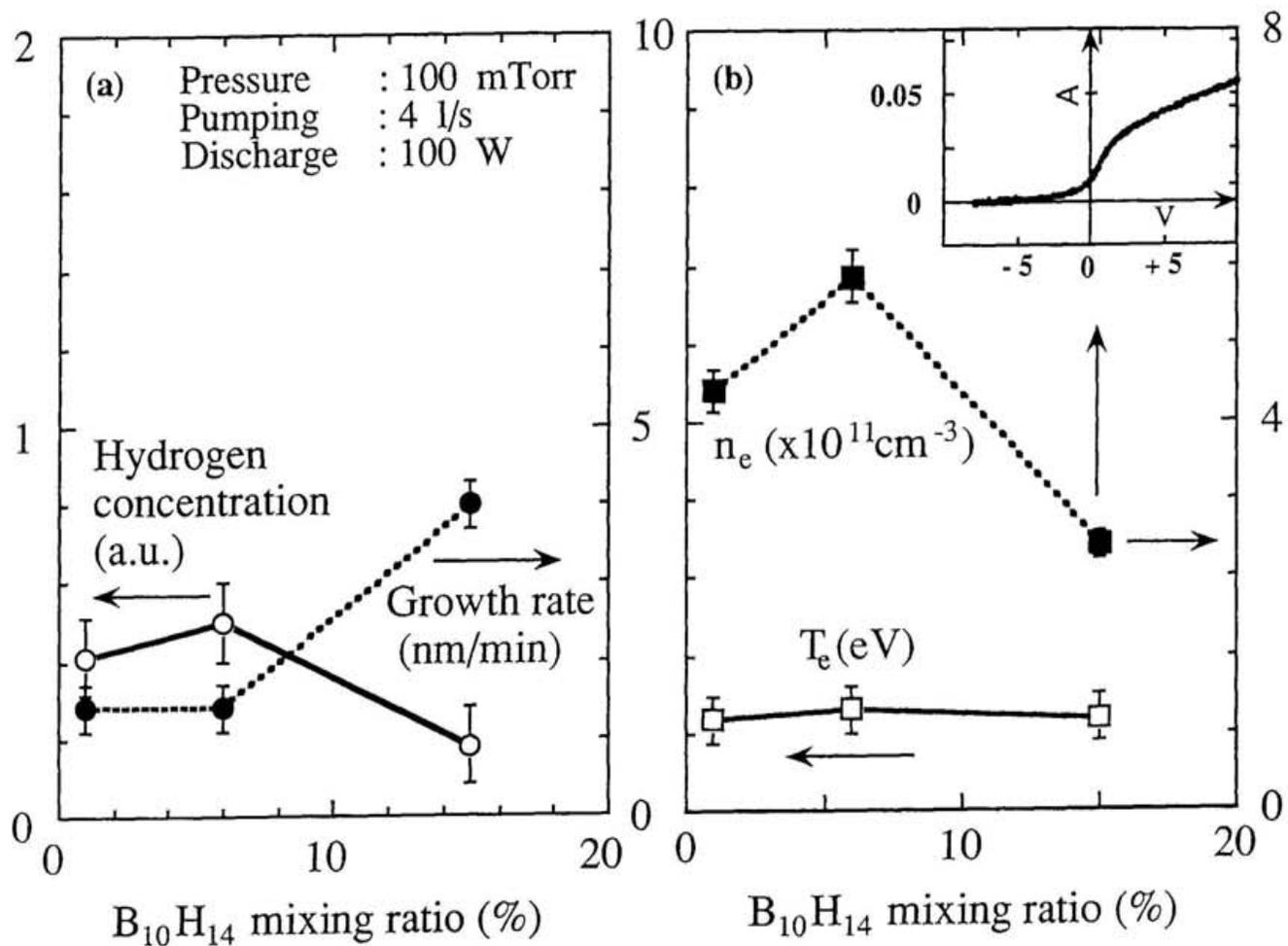
Fig. 13. The mixing ratio R dependence under standard condition of
(a) the hydrogen content and the film growth rate, and
(b) the electron temperature and density.

species, which is responsible to film formation, might be also high, resulting increase of the film growth rate with decrease of hydrogen content.

*Total pressure dependence with constant flow rate*

In Fig.14 (a) and (b), the hydrogen contents clearly decrease with decreasing total pressure. This result is in good agreement with previous observations in monosilane and carbon coating [2,3]. In Fig.14 (b) the electron temperature increases with decrease of the total pressure. At this time the flux of radical species containing decaborane is presumed to increase, resulting in high growth rate of boron film with low hydrogen concentration.

*Flow rate dependence with constant pumping speed*

In order to make clear the effect of $B_{10}H_{14}$ gas flow rate on hydrogen concentration, two kinds of experiments on flow rate dependence without changing the mixing ratio, that is one with fixed pumping speed and the other with fixed total pressure were carried out. In contrast to the previous report in $B_2H_6$ flow rate dependence carried out at $200^oC$ [4], in both cases our results gave lower hydrogen content at lower decaborane flow rate as shown in Fig. 15 and Fig. 16. One of possible reasons for this discrepancy might be difference in experimental conditions. In this experiments, the flash desorption filament was in floating potential to prevent heating up of the boron film without bombardment of ions in the energy of cathode potential around 300V. But the temperature of flash filament was not measured. In this condition liner temperature during boronization is $70^oC$. In Fig. 15, hydrogen content decreases with decreasing flow rate at a constant pumping speed and pressures varied. When the $B_{10}H_{14}$ flow rate is low and the discharge
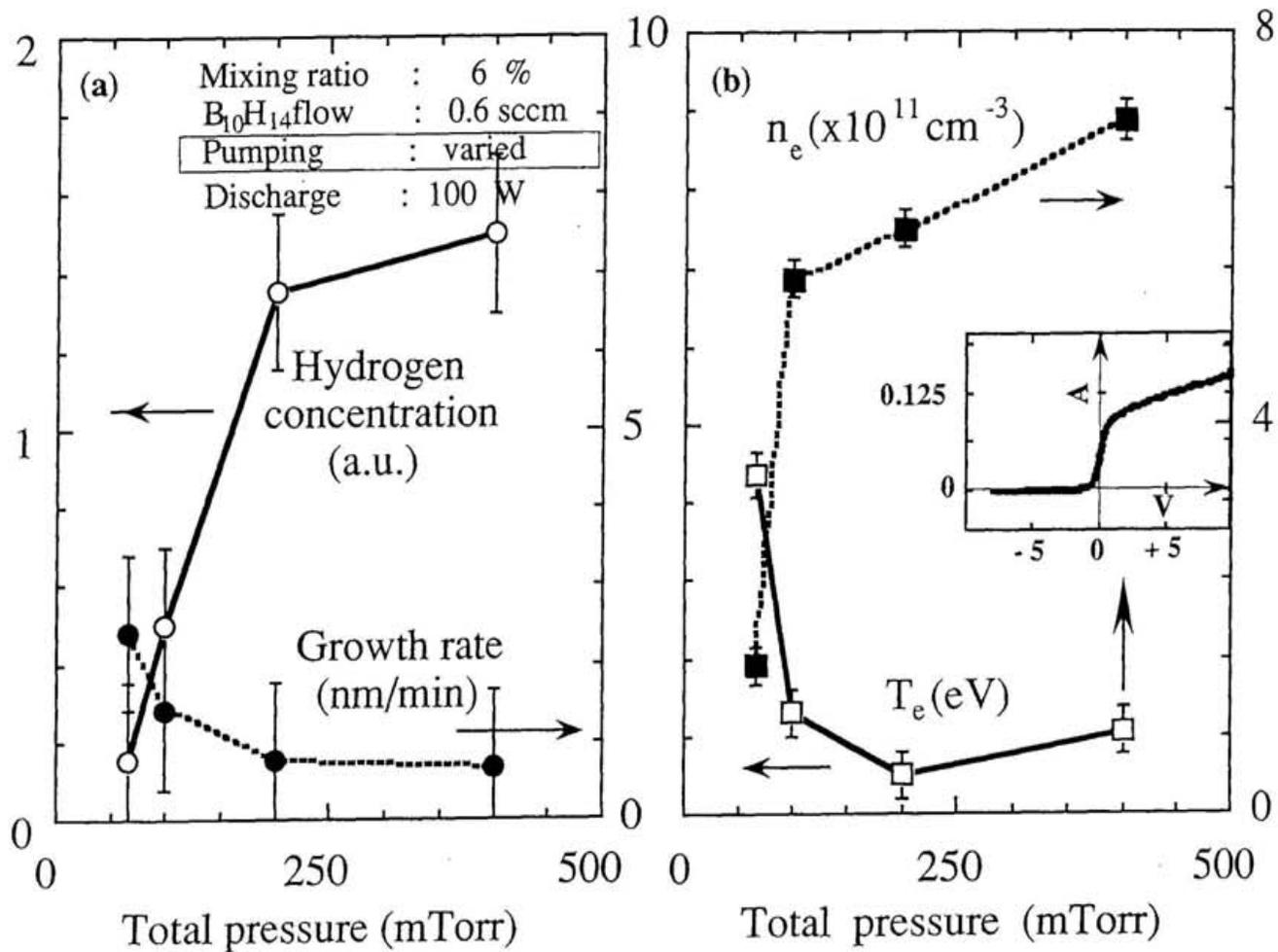
Fig. 14. The total discharge pressure P dependence with constant flow rate Q
of (a) the hydrogen content and the film growth rate, and
(b) the electron temperature and density.
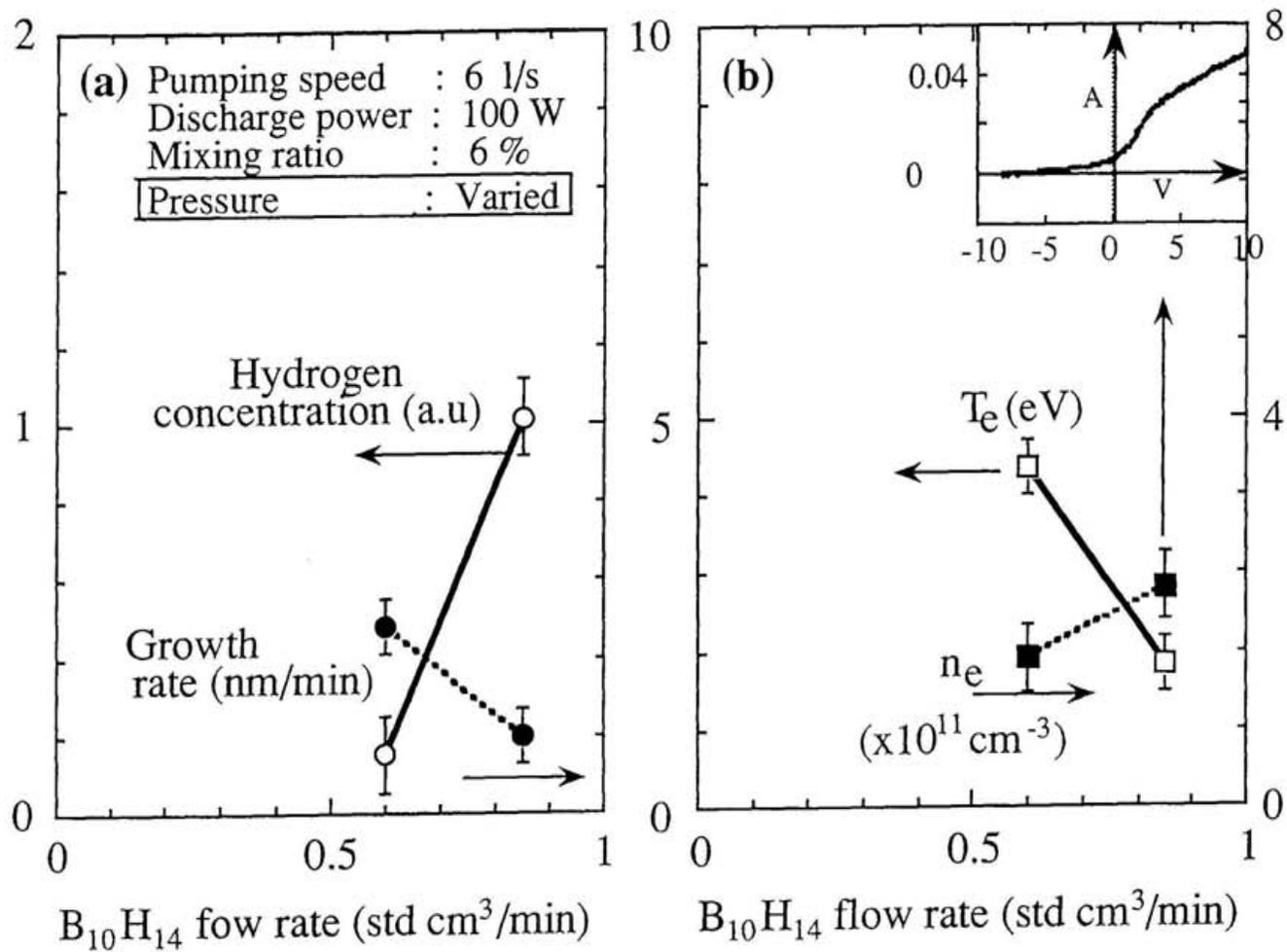
Fig. 15. The decaborane flow rate Q dependence with constant pumping speed S
of (a) the hydrogen content and the film growth rate, and
(b) the electron temperature and density (pressure varied).
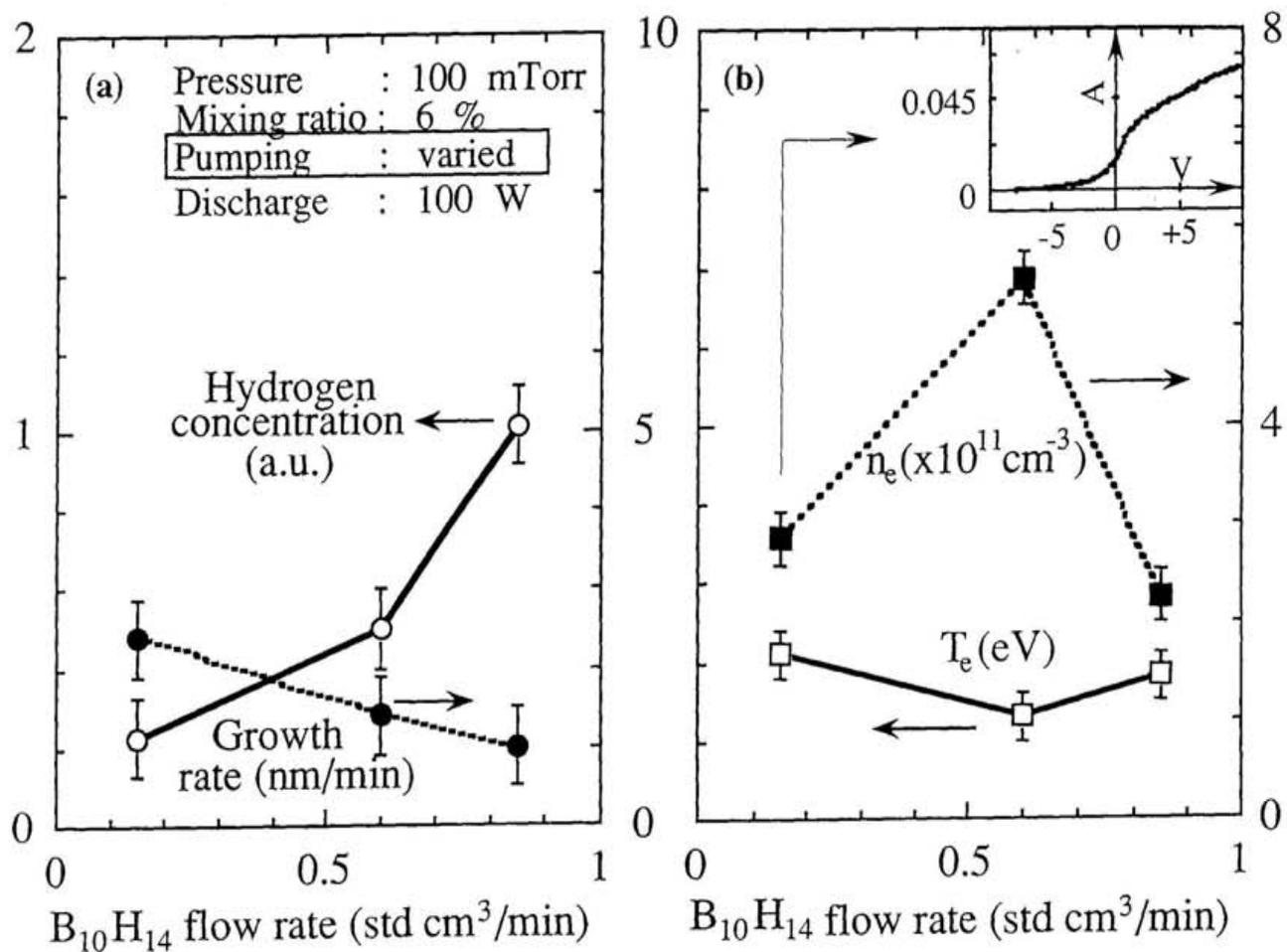
Fig. 16. The decaborane flow rate Q dependence with constant pressure P
of (a) the hydrogen content and the film growth rate, and
(b) the electron temperature and densitiy (pumping speed varied).

pressure is also low, the flux of active species which are responsible to boron film formation might be high according to pressure dependence, shown in Fig.14. In fact in Fig. 15, $T_e$ is as high at low flow rate as in Fig. 16. In Fig. 16, hydrogen content decreases with decrease of decaborane flow rate at pumping speed increased to keep the pressure constant. When the pumping speed is high, evacuation of hydrogen out of the discharge system is accelerated. Thus increase of pumping speed is presumed to prevent hydrogen incorporation. These results suggest us to use high pumping speed for suppression of hydrogen content.

## 4.2 Comparison with Coating from Methane (CH4) and Diborane (B2H6)

The results measured with FFM were also confirmed as a cross check by using RGA. Figures (5) and (6) show that signal intensities of m/e = 2 ( $H_2$ ), m/e = 27 ( $B_2H_5$ ), or m/e = 15 ( $CH_3$ ) taken with RGA versus time clearly change when the discharge is switched on. This result is explained by molecular processes such as ionization and dissociation of diborane or methane gases in discharge not in the RGA apparatus having a hot filament.

Table 1. The discharge power dependence of H/B or H/C, deposition ratio measured with residual gas analysis.

| Starting gases | Discharge Power (W) | Deposition ratio of B or C | H/B or H/C in film |
|---|---|---|---|
| $B_2H_6$ | 80 → 200 | 0.62 → 0.79 | 2.29 → 1.68 |
| $CH_4$ | 80 → 200 | 0.41 → 0.57 | 3.44 → 2.60 |

By using eqs.2-6 and 2-7, the RGA results in Table 1 show that both H/B and H/C ratios decrease with the increase of the B or C deposition ratio, namely the film growth rate, by increasing the discharge power as observed in Figs. 17 and 19 with FFM. Since the value $\beta$ is actually not easy to evaluate experimentally, here we supposed $\beta = 1$, which represents complete dissociation of hydrogen atoms from working gas molecules. Therefore RGA is only used in this study as a complementary method to relatively support the FFM results within experimental errors.

### 4.2.1 Carbon Coating with Methane (CH4)

It is observed in the Figs 17 and 18 that the films prepared with pure methane $CH_4$ result in low hydrogen content with high growth rate. These results are in good agreement with findings in the previous results on the boron film produced with $B_{10}H_{14}$.

In Fig.17, the hydrogen content decreases as discharge power increases. As listed in the figures, the discharge conditions on discharge power dependences are as follows; the total pressure of 60 mTorr, flow rate of 9.64 sccm for $CH_4$, and pumping speed of 2 l/s for He.

From Figs. 18, it can also be seen that the hydrogen content decreases with the increase of the total pressure. As listed in the figure, the discharge conditions on total gas pressure dependences are as follows; discharge power 100 W, flow rate varied with 9.64 sccm for $CH_4$, and pumping speed of 2 l/s for He.
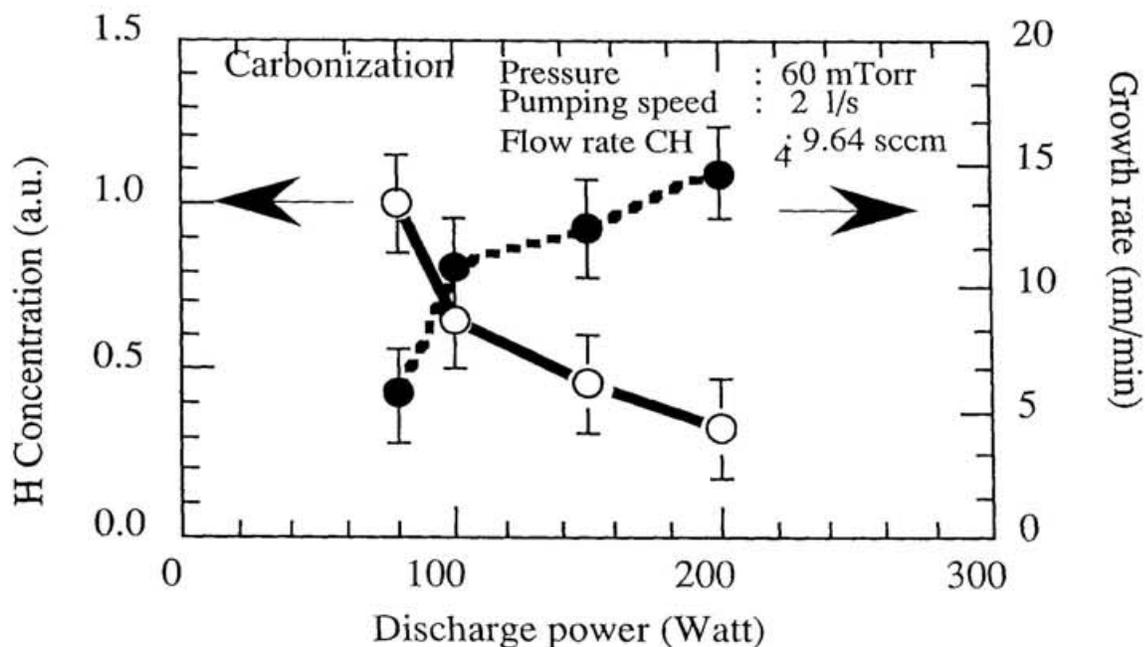
Fig. 17. H concentration and growth rate of carbon film
prepared by CH $_4$ as a functions of ( a ) discharge power,
H concentration is normalized by highest value
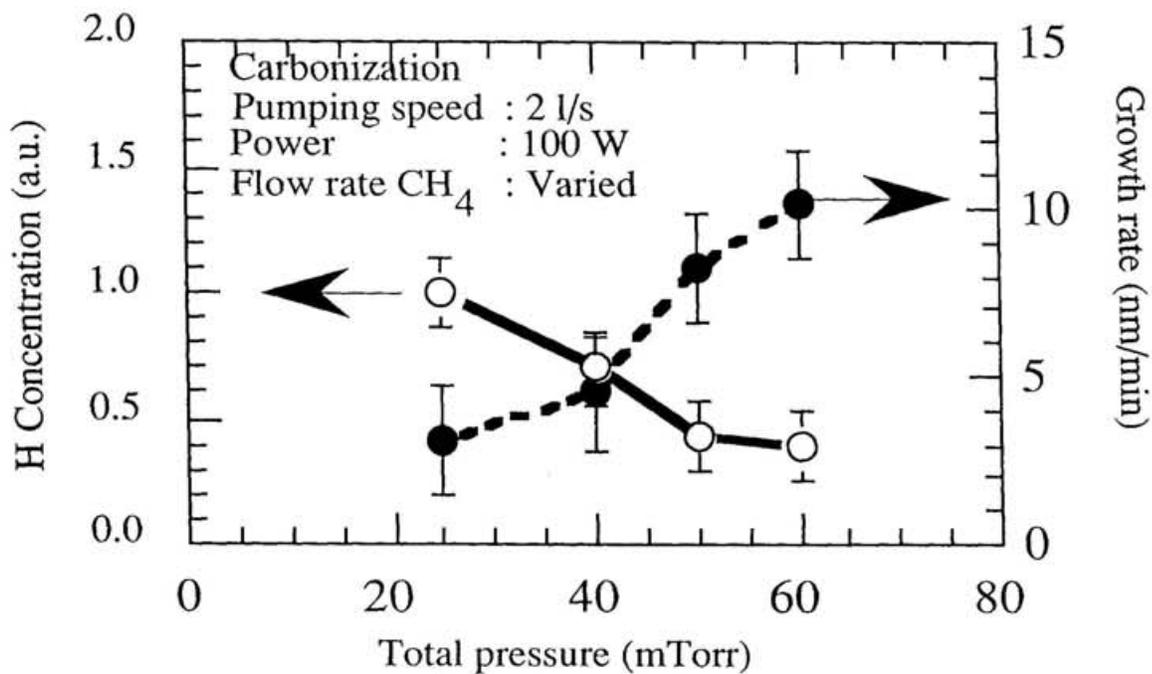


Fig. 18. H concentration and growth rate of carbon film
prepared by CH $_4$ as a functions of total pressure.
H concentration is normalized by highest value

### 4.2.2. Boron Coating with Diborane ($B_2H_6$)

It is observed in Figs.19 and 20 that the films prepared with $B_2H_6$ result in low hydrogen content with high growth rate. These results are in good agreement with findings in the previous work on the boron film produced with $B_{10}H_{14}$.

In Figs.19, the hydrogen content decreases as discharge power increases. As listed in the figures, the discharge conditions on discharge power dependences are as follows; the total pressure of 100 mTorr, mixing ratio of 5 % with flow rate of 24.2 sccm for $B_2H_6$ and 15.5 sccm for He, pumping speed of 4 l/s for He.

From Fig. 20 also can be seen that the hydrogen content decreases with the increase of the total pressure. This result in a good agreement with previously found in reference [4]. As listed in the figures, the discharge conditions on total gas pressure dependences are as follows; discharge power 100 W, mixing ratio of 5 % with flow rate varied of 24.2 sccm for $B_2H_6$ and 15.5 sccm for He, pumping speed of 4 l/s for He.

## 4.3. Dependence on Electrical Potential of Substrate

In the previous works the H content were measured by flash filament method or residual gas analysis (RGA), and the FF was set at electrically floating potential to avoid heating up to discharge current. Here, to make clear influence of electrical potential of FF, boron films were produced on floating or cathode potential samples, and H content and depth profiles of H were analyzed with ERD technique. For this purposes, new modified method using RBS was established to monitor the probing ion flux as shown in eq.2-2.
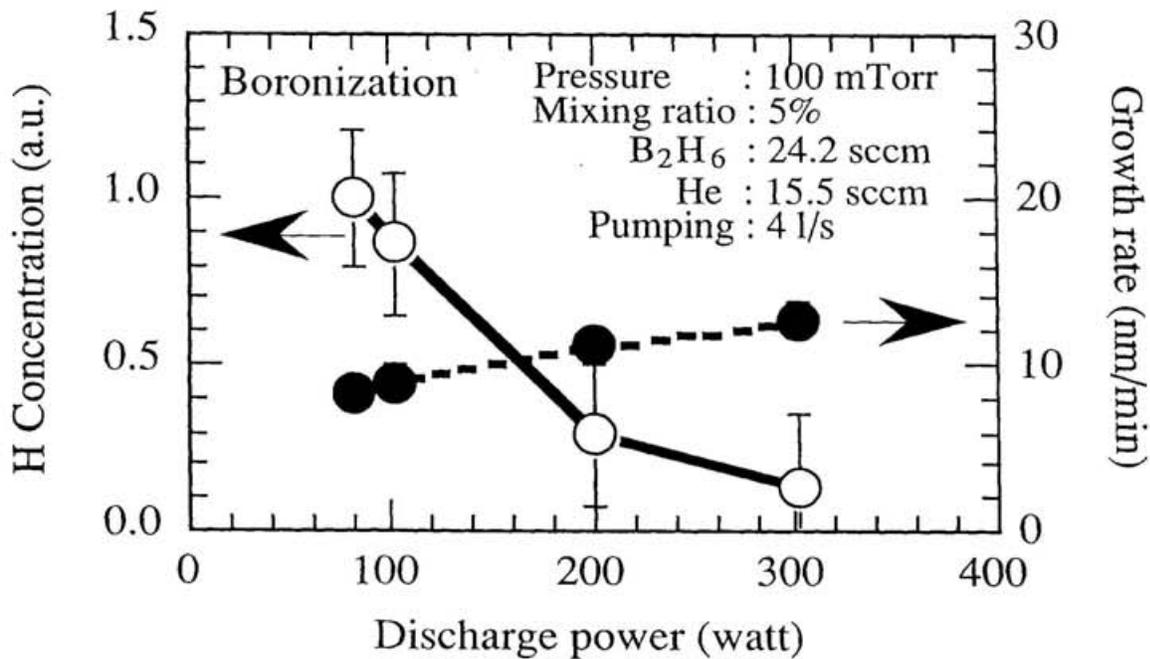
Fig. 19. H concentration and growth rate of boron film
prepared by $B_2H_6$ as a functions of discharge power,
H concentration is normalized by highest value.
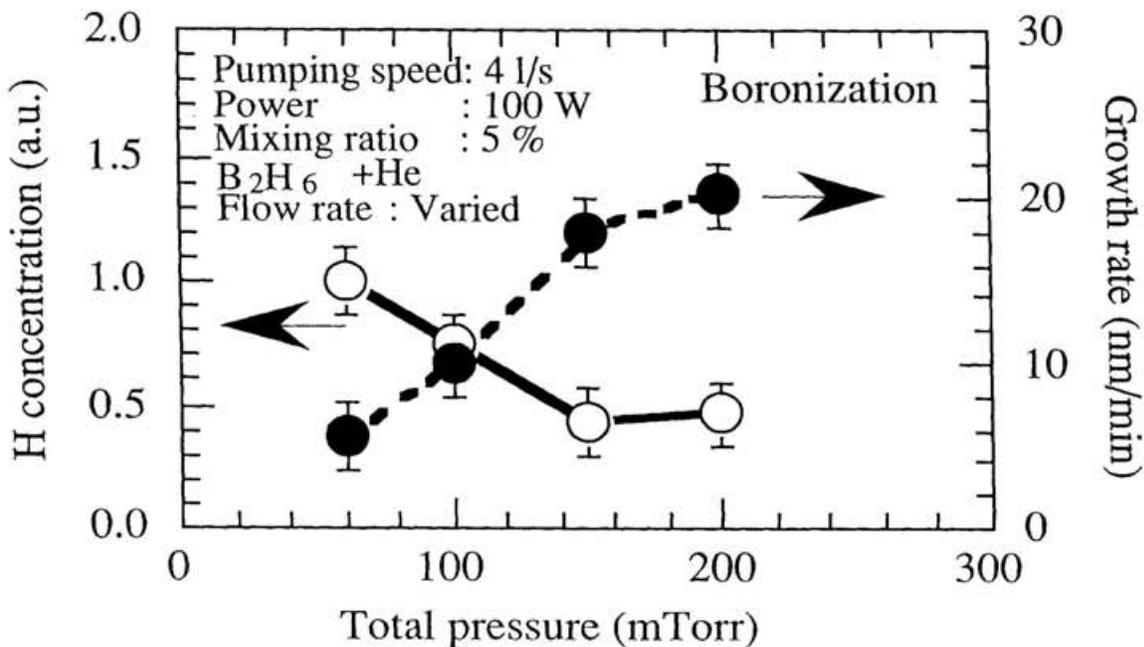


Fig. 20. H concentration and growth rate of boron film
prepared by $B_2H_6$ as a functions of total pressure,
H concentration is normalized by highest value

### 4.3.1 Boron Films Thickness

Figure 21 shows a typical RBS spectrum taken from the cathode potential B coated Al sample, on which B cannot be clearly observed, probably due to surface roughness of Al target. However, the B film thickness was measured from the shift of the Al surface edge as shown in Fig. 21. The results of the film thickness given by quartz crystal monitor was confirmed with RBS measurement. The film thickness $d_f$, estimated by RBS, is similar to quartz crystal monitor, the difference is within the experimental error of about $\pm 10$ %.

### 4.3.2 Hydrogen Depth Profiles

Figure 22 shows the typical hydrogen depth profiles in boron films formed on floating or cathode potential Al samples. From this figure it is observed that the H profile on the cathode potential sample is more dense, flat, and thick in comparison with the floated one. The peak of the hydrogen distribution for floating sample potential was at about 40 nm, and shows that the incorporation of hydrogen is low for films deposited at floating sample potential in DC glow discharge. This result was also supported by recent experiments in ECR discharges where the dependence of H concentration on the electric biasing voltage of the substrate was measured [5,6]. The accuracy of depth profile was about 100 Å.

Figures 23 (a) and (b) show the peak H/B atomic ratio and the film growth rate measured with ERD and RBS as a function of the discharge power or total gas pressure, respectively. From both figures it can be observed that the H/B are reduced with increasing the film growth rate when the discharge power is increased, or when the total pressure is increased. These results are in good agreement with the results obtained

**Discharge conditions**
Total pressure      : 200 mTorr
Discharge power : 100 Watt
Mixing ratio      : 5 %
   ( $B_2H_6$/ He )
Deposition time   :13 min
Sample temp.    ~ $90^{o}C$
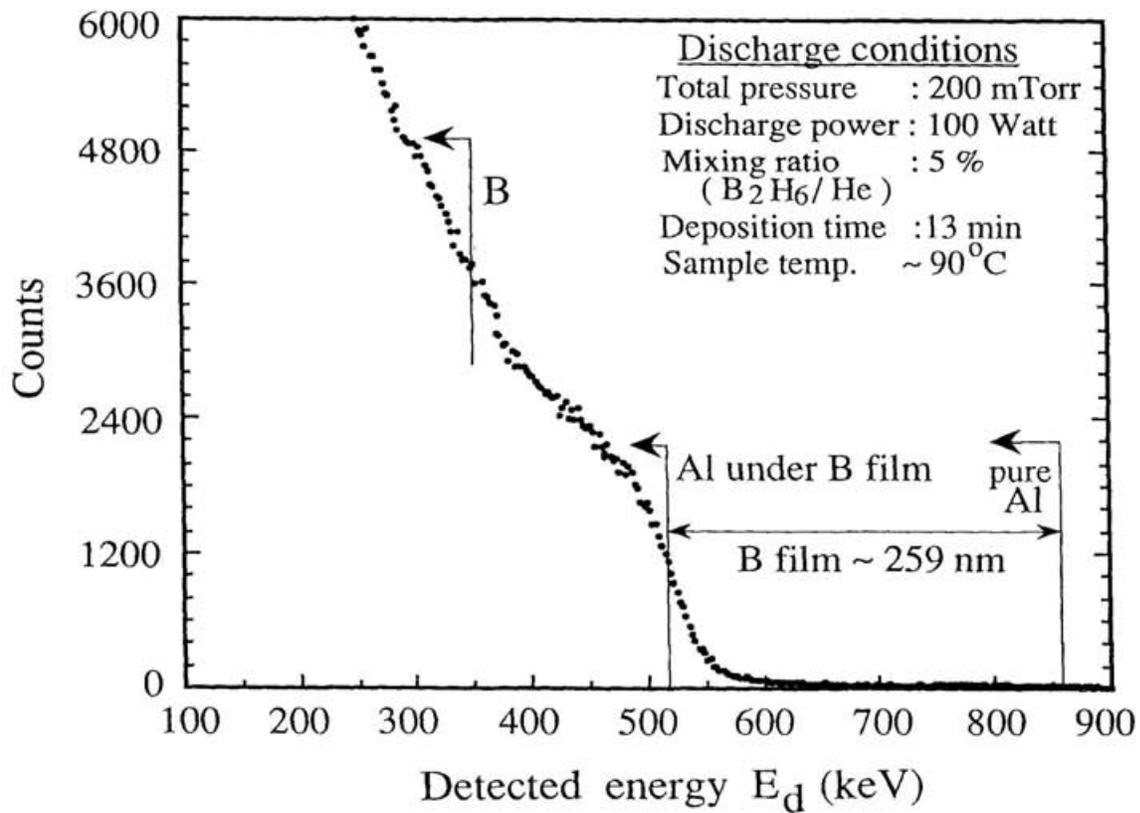
Fig. 21. RBS spectrum taken from B film prepared on the electrically
     cathode potential Al sample, and the schematic illustration
     of the ion beam analysis system.
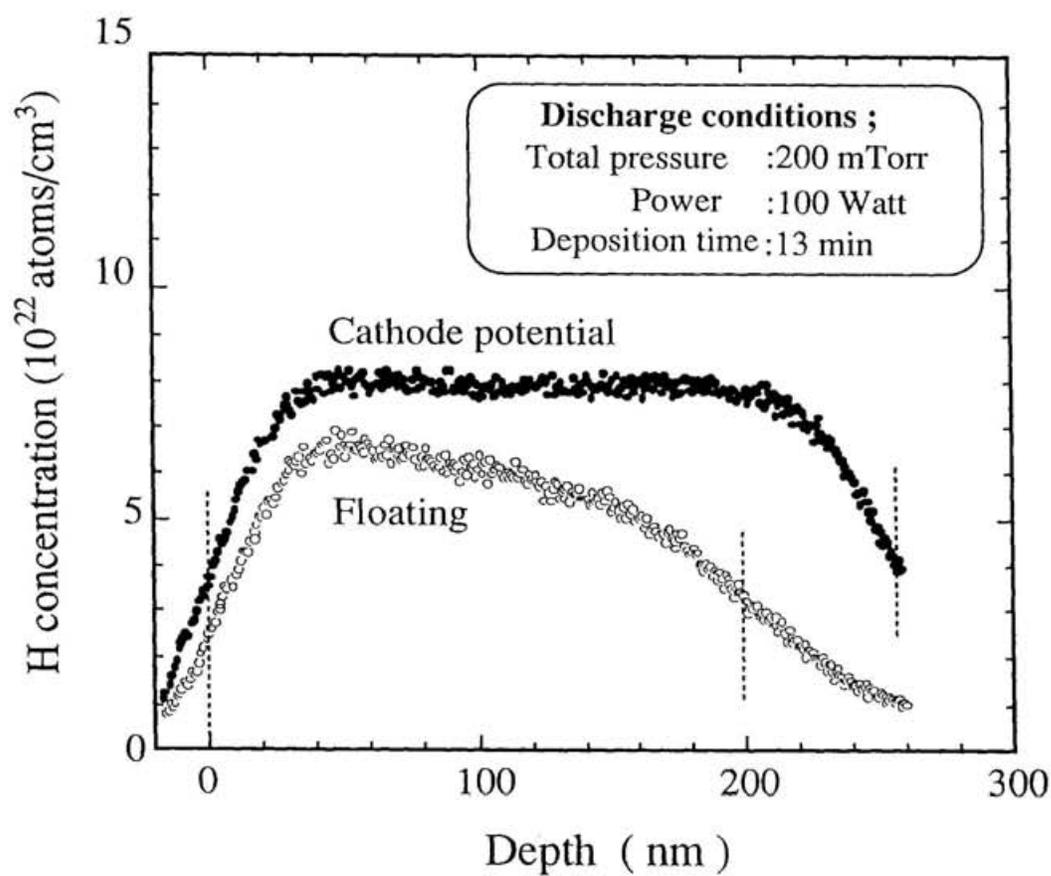
Fig. 22. Depth profiles of hydrogen atom in boron film on electrically floating or cathode potential Al samples.

so far from the FF method or RGA. Here, it should be noted that sample temperatures during boron coatings were about $90^{\circ}C$ at maximum as shown in Fig. 8, but only the temperatures of both samples in case of 300 W discharge were about $140^{\circ}C$ at maximum, at which temperature the heating effect during discharge could not negligible for desorption of H according to ref. [7].

### 4.3.3 Effect of Sample Potential

The film growth rate gives the B atoms flux $\Phi_{BC}$ and $\Phi_{BF}$ for cathode potential and floating cases, respectively. We speculate that $\Phi_{BC}$ consists of neutrals, that is, radicals and energetic $B_nH_m$ ions, but $\Phi_{BF}$ mainly consists of radicals, because, under glow discharge, ions are mainly produced in the cathode dark space due to electron impact and they are mostly extracted to the cathode surface which has deeper negative potential of about 500 V than that of a several V on the floating sample. Therefore $\Phi_{BC} - \Phi_{BF}$ may give B atoms flux in forms of $B_nH_m^+$. Standing on this speculation, Fig. 24 (a) and (b) show that the H/B ratio is reduced with reducing the ionic flux ($\Phi_{BC} - \Phi_{BF}$). It is also shown that, though the ionic flux contributes to increasing the film growth rate as shown in Fig. 23, it is better to increase the radical flux $\Phi_{BF}$ for reducing the H/B ratio.
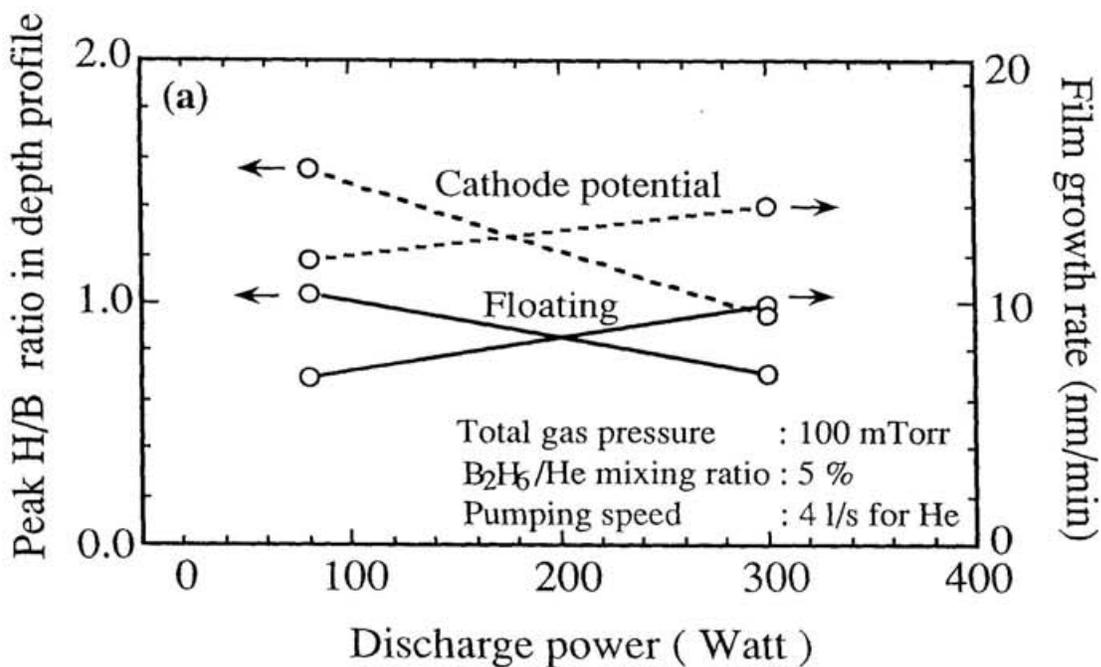
Fig. 23 (a). Discharge power dependence of H/B peak ratio in depth profile and growth rate on the floating or cathode potential Al samples.
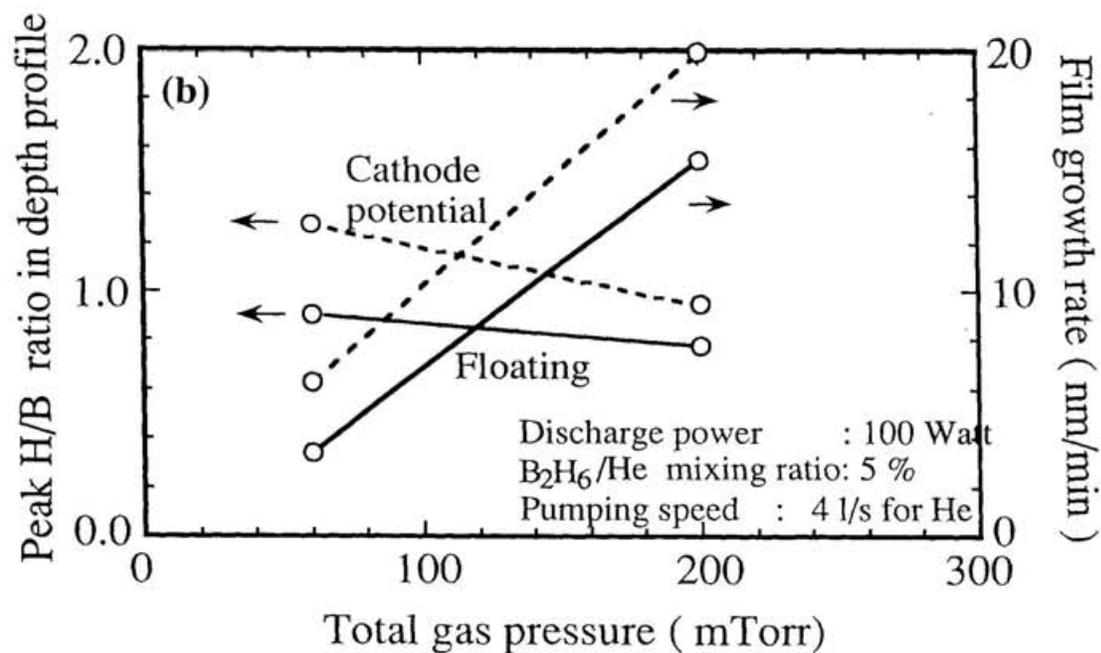


Fig. 23 (b). Total gas pressure dependence of H/B peak ratio in depth profile and of growth rate on the floating or cathode potential Al samples.
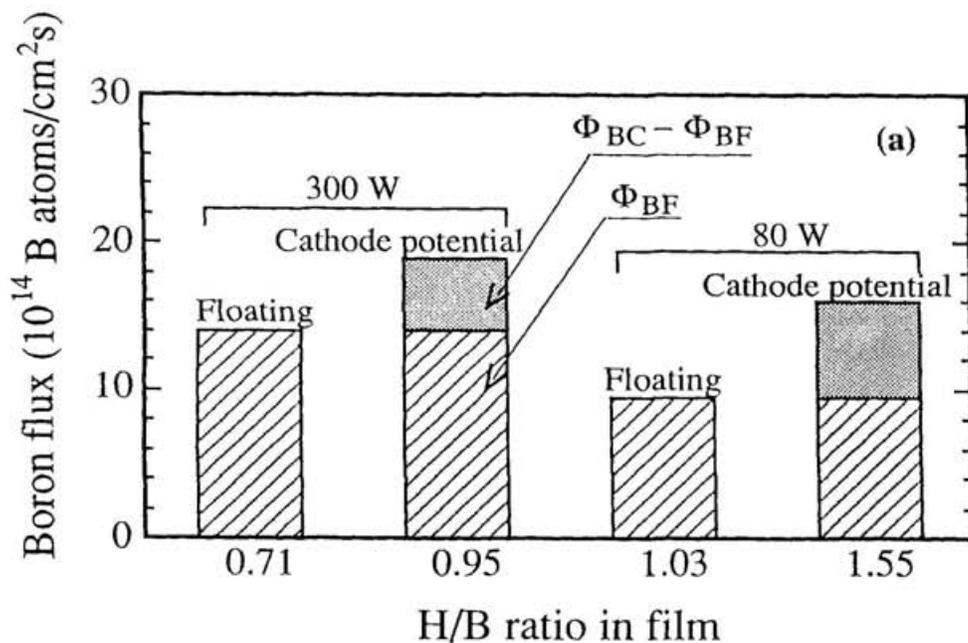
Fig. 24(a). Relation between the H/B ratio and the B molecules fluxes $\Phi_{BC}$ and $\Phi_{BF}$ on the floating or cathode potential Al samples, respectively, under the discharge power dependence.
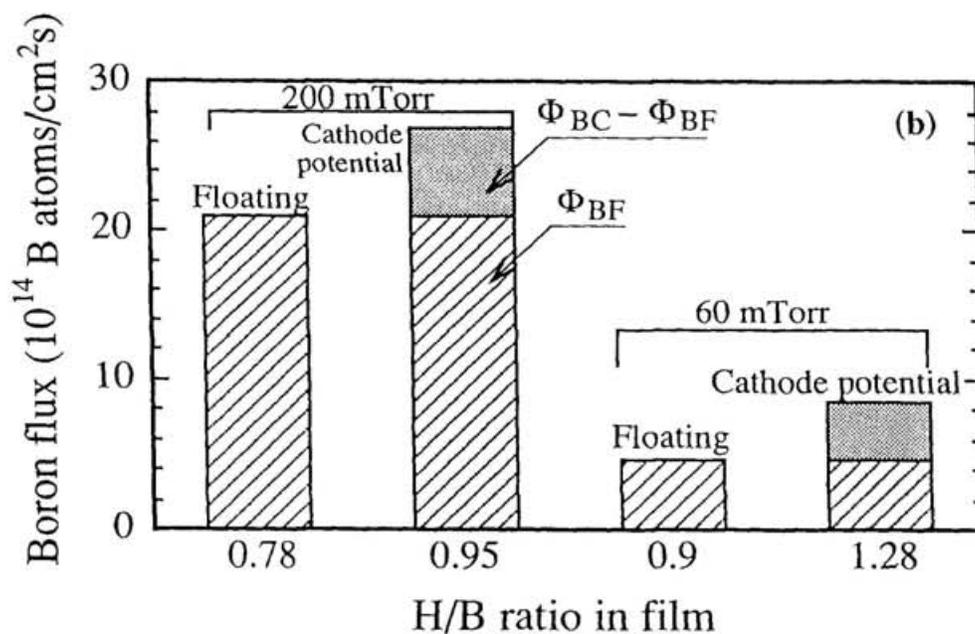


Fig. 24(b). Relation between the H/B ratio and the B molecules fluxes $\Phi_{BC}$ and $\Phi_{BF}$ on the floating or cathode potential Al samples, respectively, under the total discharge pressure dependence.

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# Chapter 5

# Modelling under Experimental Findings

## 5.1 Common Features in Measured Results[1]

Experimental dependence on each DC glow discharge parameters for obtaining boron films with low hydrogen content with high growth rate are summarized in Fig. 25 for the case of decaborane. In common, the results can be observed that the hydrogen concentration was relatively low when the film growth rate was high.

## 5.2 Mechanism of Hydrogen Reduction

During boronization or carbonization, the surface of the depositing materials is continually bombarded by plasma generated species including ions, radicals, and other molecules. Little is known concerning the dynamic interaction of any of these species with surface, although it is clear that some subset of these encounter lead to depositions. Some individual molecule/surface collisions may result in film growth by an attachment reaction or removal of previously attachment atoms. These processes can be seen in Fig. 26.

A simple model of film growth and hydrogen reduction is proposed as follows. If it is assumed that BH is the species responsible for film growth, it can be proposed the reaction in the deposition of B film from diborane is;

$$B_2H_6(gas) \xrightarrow{\text{ignition}} 2B{:}H \text{ (film)} + 2H_2(gas) \ , \qquad (5\text{-}1)$$
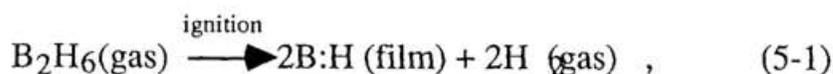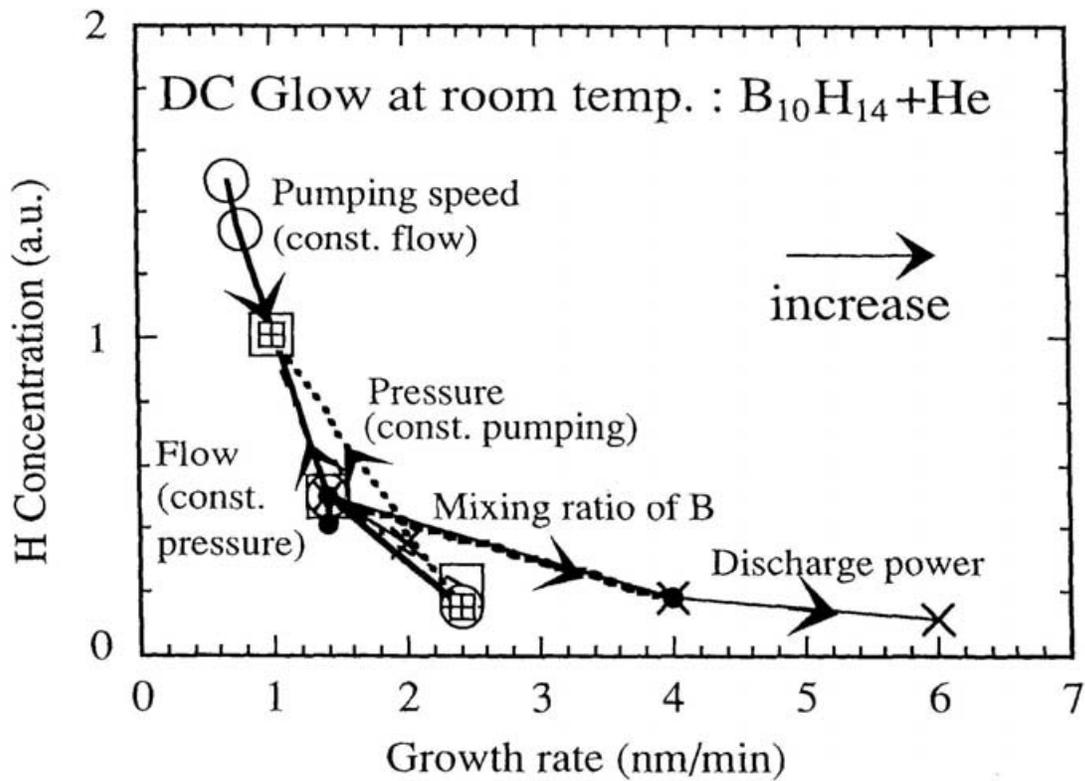
Fig. 25. Relation between H concentration and film growth
rate measured in boronization with $B_{10}H_{14}$ under
variuos dependence on discharge conditions
( discharge power, total pressure, flow rate,
mixing ratio, and pumping speed ).
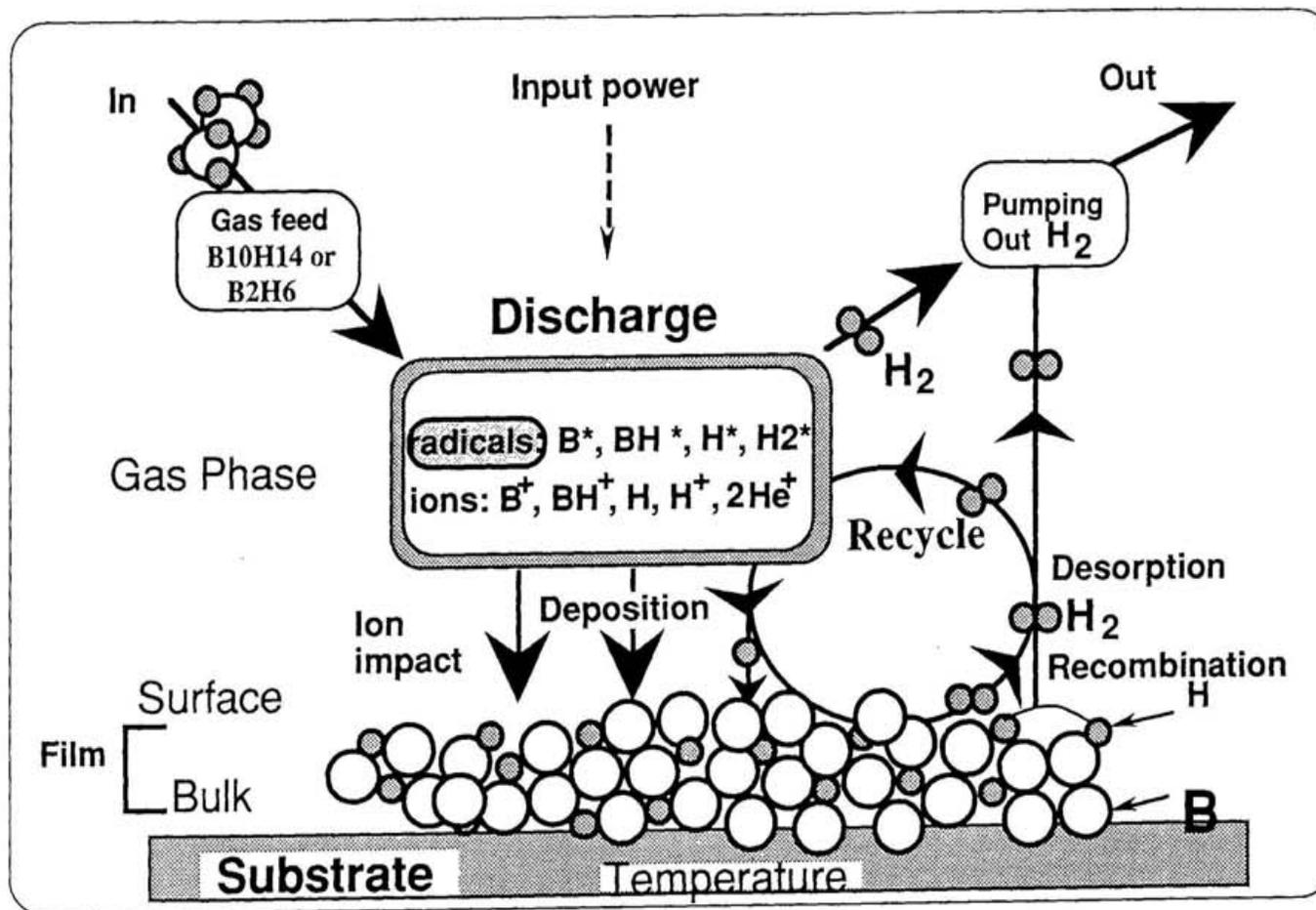
Fig. 26. A model of hydrogen reduction during
the glow discharge deposition of B film

After ignition of the discharge the diborane intensity is quickly reduced and the hydrogen intensity is quickly increased due to H molecule broken from diborane gases and stabilized during the whole deposition processes.

First, dissociated, excited and/ or ionized molecules or atoms have been known to be important parts for growing film formation. Therefore, the main effect of increasing power is to enhance these molecular processes with producing dissociated H from working gases. Thus, increasing growth rate of film formation results in low H content as shown in Fig. 17 for ($CH_4$) and Fig. 19 for ($B_2H_6$) as well as Fig. 25.

Secondly, the effect of pressure seems to be rather complicated. In case of decaborane, low pressure resulted in high electron temperature, which leads the high degree of the molecular processes and results the high growth rate with the low H content as shown in Fig. 25. On the contrary, in Figs. 18 for ($CH_4$), Fig. 21 for ($B_2H_6$), and Fig. 23 for decaborane higher pressure results in the lower H content. Mechanisms on pressure dependence is not clear within these experiments. However, it is also true in Figs. 18, 20, and 25 that higher growth rate of films leads lower H concentration.

Thirdly, many dissociated and/ or ionized products such as H, B, $BH_x$, $B_2H_x$, $B_mH_x$ (m=1~10, x=1~14) and C, $CH_x$ are expected in discharges. Here recombination may also occur among H atoms in gas/ plasma phase and on the coating surface, giving rise to increase of $H_2$ pressure. Then, higher pumping speed results in lower H content as shown in Fig. 25.

To explain the difference between ions and radicals regarding growth of B film and reduction of H/B ratio, there must be considered

two aspects, that is, the difference of molecular forms concerning B and H, and the difference of surface reactions such as impact desorption, recoil implantation and/or surface recombination of H atoms depending on kinetic energies of impinging particles including $He^+$ ions. Within this work it is not easy to evaluate these aspects quantitatively, and more detailed experiments will be needed, comparing with complementary modeling calculations.

## References

[1] M.Natsir, K.Tsuzuki, A.Sagara, and O.Motojima, Transaction of Fusion Technol., 27 (1997) 527-531.

# Chapter 6

# Conclusion

Aiming at control of hydrogen recycling, which is one of key issues to achieve high plasma performance in LHD, reduction of hydrogen contents in low Z coated films at room temperature has been systematically investigated by using the newly developed in-situ hydrogen analysis method with flash filament and the improved method with residual gas analysis as a complementary method.

Within experimental results on boron films produced from $B_{10}H_{14}$ or $B_2H_6$ and carbon films from $CH4$, the hydrogen content is successfully reduced with the increase of the film growth rate by controlling DC glow discharge conditions: as practical conditions in case of decaborane, for instance, higher power of discharge and lower pressure of working gases with higher pumping speed are better to reduce H concentration in films. These results form an important database for general use of hydrogen reduction in low Z films coated at room temperature.

The boronization experiments conclude that hydrogen content in the film formed at room temperature can be reduced by controlling discharge conditions. These results can be applied for first wall conditioning in present day plasma machines which can not relay on thermal desorption of incorporated hydrogen.

(1) The following conditions are recommended to reduce hydrogen content; low flow rate with high mixing at low pressure under high pumping speed and high discharge power within a condition to keep discharges stable.

(2) The hydrogen content can be suppressed by high growth rate of boron film formation.

(3) Concerning Langmuir probe results, it is not easy to directly discuss the relations between hydrogen concentration and the electron density or electron temperature within this work. However, it seems that when $T_e$ is high with low $n_e$, hydrogen concentration becomes low probably due to increase of boron contained radicals.

It is presumed that the hydrogen content in coated films mainly depends on both processes of molecular dissociation and/ or ionization resulting in  deposition of coating gas and atomic recombination resulting in evacuation of $H_2$ gas. The hydrogen concentration in boron films prepared with DC glow was analyzed by using elastic recoil detection method (ERD) and a new modified normalizing technique with Rutherford back scattering (RBS) was introduced.

There were obtained two important results. The first is that the floating surface is better to reduce H/B ratio. From this result it is conjectured that energetic ions flux should be reduced but the radical one should be increased. The second is that higher growth rate of B film formation gives lower H content.

The results measured with FF method also confirmed the consistency of the experimental data set obtained by using RGA and ion beam analysis with ERD. They showed a good agreement with FF. Therefore, it is concluded that flash filament method is a usable method for quick and in-situ measurement in coated film.

# ACKNOWLEDGMENTS

Appendix 1 Variation of the electron temperature (eV) and electron density
(cm$^{-3}$) measured as functions of a) power and b) pressure
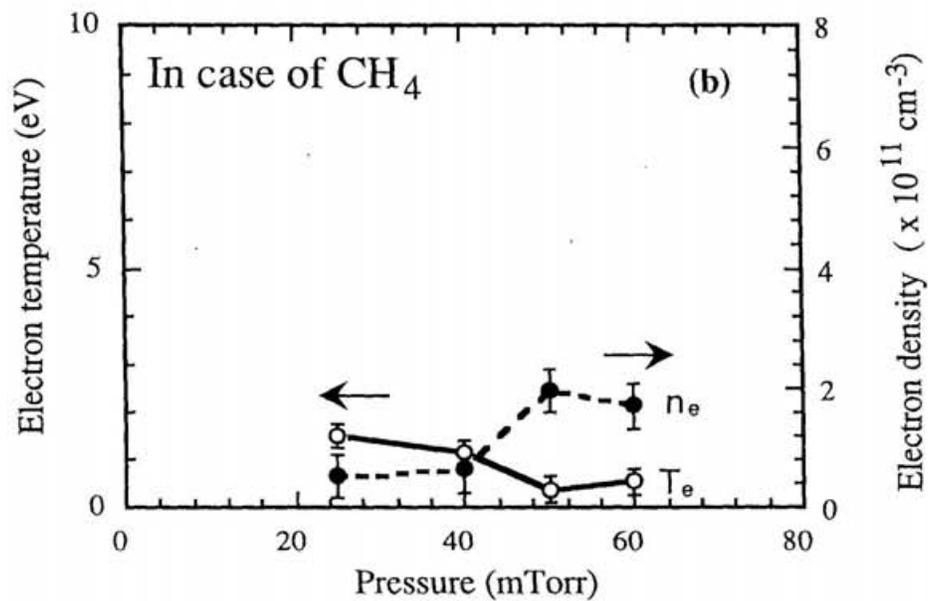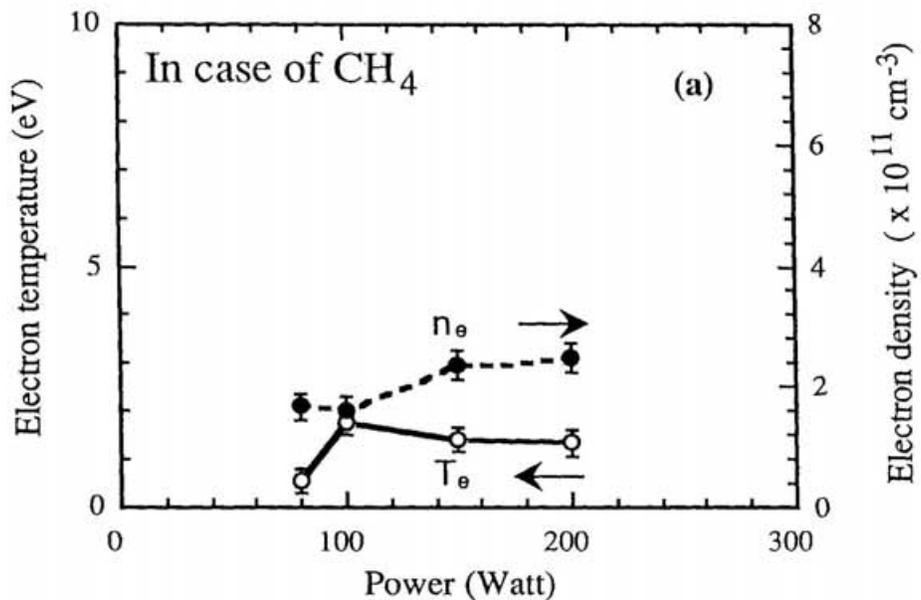
Appendix 2  Variation of the electron temperature (eV) and  electron density
(cm$^{-3}$) measured as functions of  a) power and b)  pressure
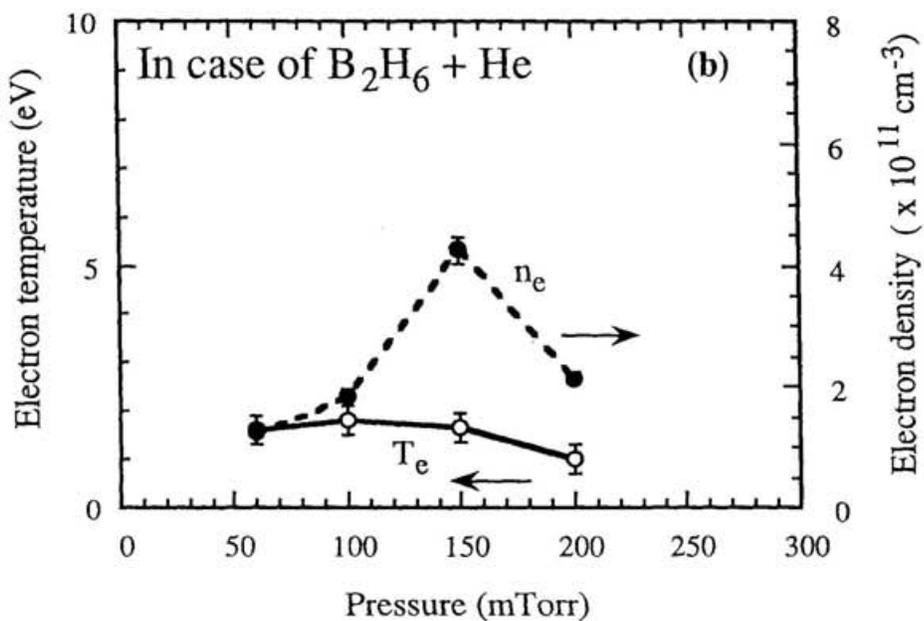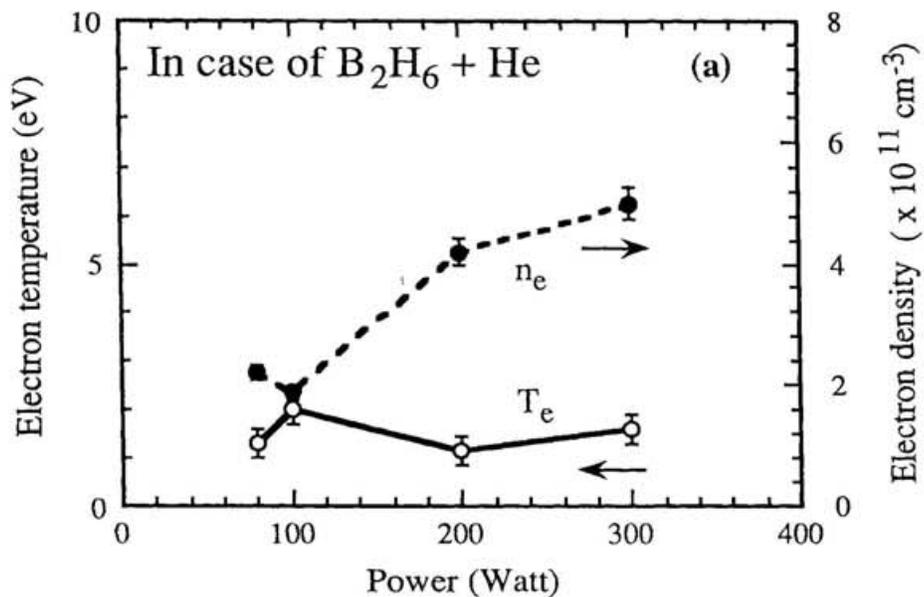
Appendix 3   Variations of ratio of emission intensities
of B2H6 and CH4 with Power



(a) Ratio of emission intensities of $B_2H_5$ (%) ($\Delta P/Po$) vs Power (watt). In case of $B_2H_6 + He$

(b) Ratio of emission intensities of $CH_3$ (%) ($\Delta P/Po$) vs Power (watt). In case of $CH_4$ (pure)