Master thesis

Effects of surface treatments

on the retained dose of impurities for plasma doping

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Introduction
Plasma Doping
for
Ultra shallow
Junction

1.1   Background

Today, IT (Information Technology), such as desktop application, mobile application and etc. has come into rapidly wide use recently, this is one of the most important technologies in our society. Development of IT owes to the improvement of semiconductor technology, mainly; Large Scaling Integrated circuits (LSIs) technology because there is no way about signal processing of GHz class at cheep, lightweight and low power without LSIs. Therefore Progress of IT must be greatly dependent on that of LSIs technology.

The progress of LSIs is caused by downsizing of devices, such as metal-oxide–semiconductor field effect transistors (MOSFETs) because high integration of the circuits become possible to carry many devices and to accomplish multi-functionalization, then high performance such as high speed and high frequency wave is realized. The downsizing of MOSFETs has been accomplished by the scaling method as shown in Fig.1.1 and Table1.1 [1]. To increase the drive current and to control the short channel effects, these scaled transistors have to be designed very carefully. In this method, lateral and vertical dimensions and supply voltage are scaled down by the same factor S, while impurity-doping concentration is increased by the factor S.

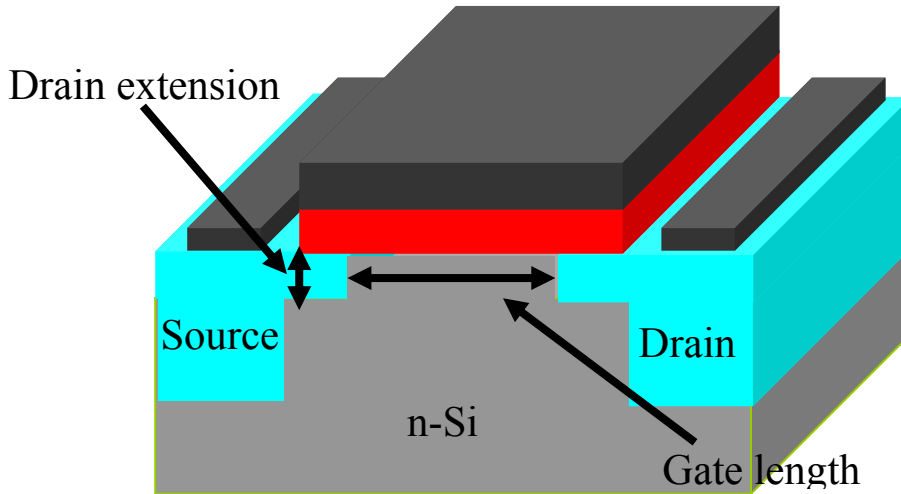| Quantity	Before Scaling	After Scaling
Channel Length	L	L/S
Channel Width	W	W/S
Device Area	A	A/S^2
Gate Oxide Thickness	t_{ox}	t_{ox}/S
Gate Capacitance (unit area)	C_{ox}	$S*C_{ox}$
Junction Depth	x_j	xj/S
Power supply voltage	V_{DD}	V_{DD}/S
Threshold Voltage	V_{T0}	V_{T0}/S
Doping Concentration	N_A	$S*N_A$
	N_D	$S*N_D$

Table1.1 Scaling of MOSFET by scaling factor of S.

Fig.1.2Schematic of P-MOSFET

1.2. Junction

1.2-(i) Requirements and problems for shallow junction

For the future small scale MOS transistors, innovations of ultra shallow junction technology are required.

As the feature size of the devices continues to shrink in both lateral and vertical dimensions, the required depth of source/drain junctions becomes shallower and shallower.

The extension region of the source/drain has to be formed very shallow in order to minimize the short channel effect while maintaining high drive current.

The plasma doping method is a promising candidate since low energy introduction of dopants with high throughput by a low cost machine system will be possible, comparing to the conventional low-energy ion implantation method[1].

However, clarifying issues concerning doping mechanism in plasma doping is necessary for precise process controllability. In the surface region of as-doped substrates, dopants localize in very sallow region with high concentration and dopants may be deposited rather than implanted. It was reported that even doping from neutral gas species was significant factor where dopants possibly adsorbed on the substrate surface [2]

Consequently, length between source and drain is nearly in other words, channel length becomes shorter, and various inconvenient influences called short channel effect is appeared.   In order to suppress problem to of short channel effect to the minimum, it is necessary to make shallower junction and to hold behavior of a long channel.   While, it is necessary to suppress raising maximum drain extension sheet resistance.

According to ITRS roadmap 2003 as shown in Table 1.5 and Fig.1.10, junction depth is 13-22 in 2005 year and 7-12 in 2010 year [2].　However, as concerns conventional ion implantation technology, cost is high and control of low energy is difficult.　Therefore, new ultra-shallow junction formation technology is demanded.
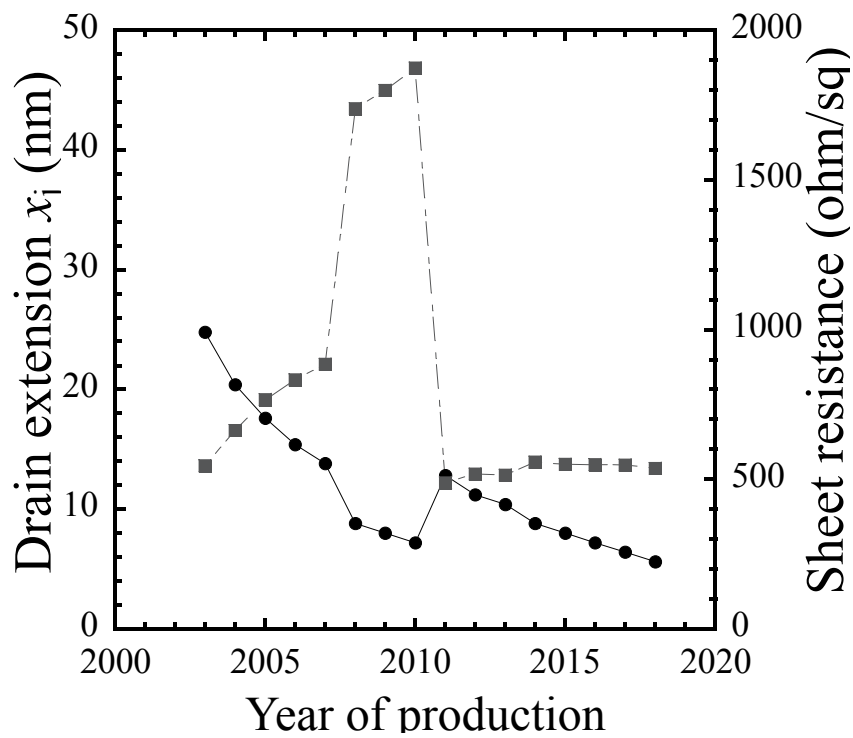
Fig.1.3 Roadmap for year of production vs. ρ_{sh}, X_j ITRS'2003

1. 2 Requirement for plasma doping (PD) method

In these years, as rapidly downsizing, conventional ion implantation technology is too difficult to control low energy implantation for ultra-shallow junction formation. And so, establishment of new ultra-shallow junction technology is required [1-10]. Plasma doping (PD) method is expected as the low cost and high performance technology as follows,

Possibility to control of implantation by low energy

High throughput

Compact system

Excellent characteristics of transistor.

Another advantage of PD method can be given isotropy and anisotropy. Herewith, 3-dimention formations such as trench sidewall can be doped.

While demerit of PD method compared with ion implantation method have as follows;

Substance without mass separation reaches Si wafer

The exact amount of ion using Faraday cup cannot be measured because only positive ion doesn't always reach Si wafer. However, neither problem is fatal. Although the former problem may have a bad influence on transistor operation, it already has report of operating one. On the other hand, although the latter problem has the point that dosage isn't known simply, simple measurement for dosage is becoming impossible in case of low energy by ion implantation method because the problem such as sputtering and back sputtering is not neglected within ultra-shallow junction. Therefore, According to ITRS roadmap 2003, PD method is expected as low energy technology as

shown in Fig.1.3 in future [2].

Fig. 1.3 IRTS roadmap 2003

Figure 1.4 shows Boron depth profile by SIMS in case of using conventional ion implantation method and plasma doping method. In the vicinity of surface, Boron concentration in case of using plasma doping method was strong that of in case of using conventional ion implantation. It is guessed that this phenomenon is absorption of Boron in neighbor of Si surface due to reacting absorption of gas phase.
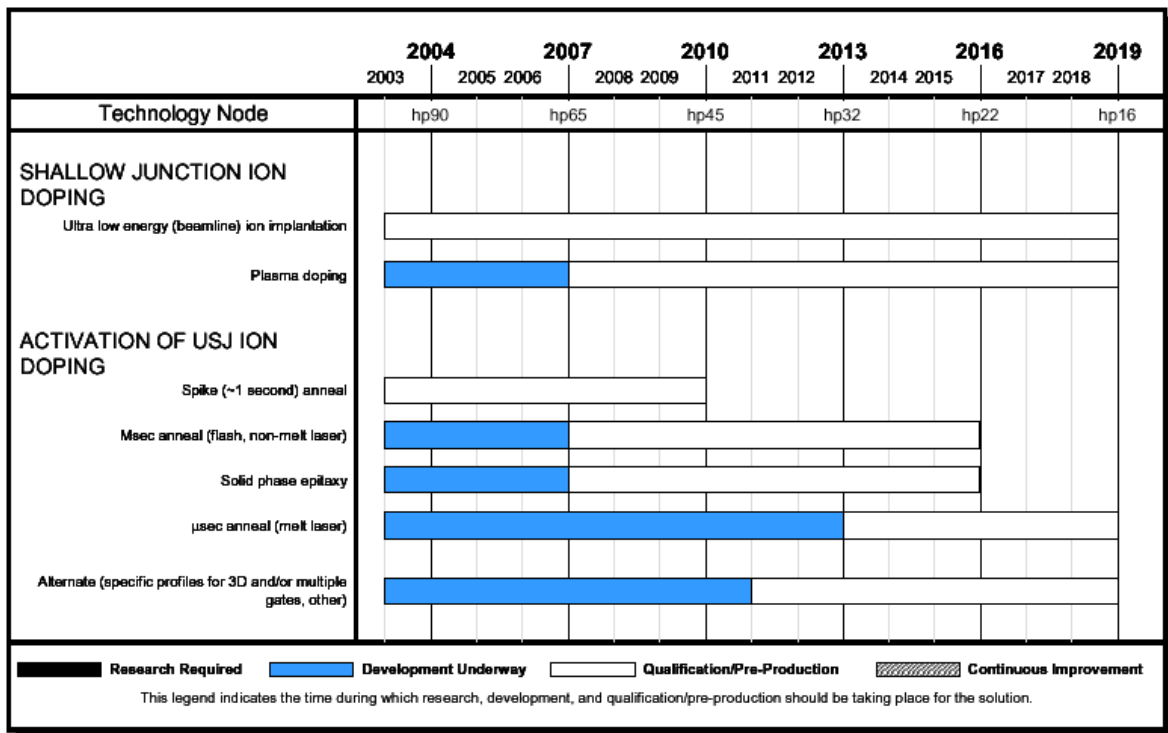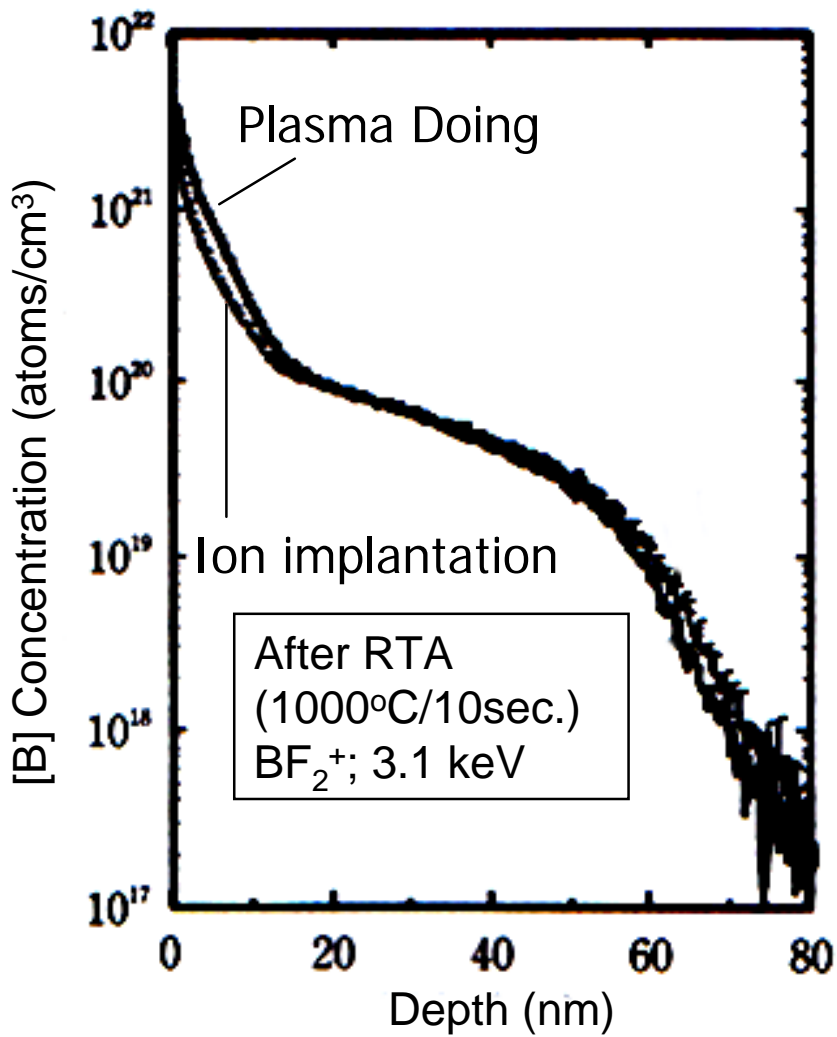

Fig.1.4 Boron depth profile by SIMS in case of using conventional ion implantation method and plasma doping method

1.4 Problem

Possible states of dopant materials introduced by plasma doping can be categorized as shown in this figure. In brief, most impurity atoms are implanted in the substrate, but significant amount of impurity atoms is adsorbed or deposited on the substrate surface.

B atoms are densely placed in the shallow surface region.

Adsorption or deposition layer may exist on the surface.

Boron atoms, however, are placed in very shallow surface region of the substrate in any case.

Therefore, the doped layer can be susceptible to post cleaning treatment. This means that it is very important to establish an appropriate post cleaning process in order to control the resulting dose of the impurities.

Iit is indispensable to establish an appropriate post cleaning process in order to minimize any effects on the doping layer.

Figure 1.5Possible states of dopants introduced
by plasma doping process

1.4 Purpose of This Study
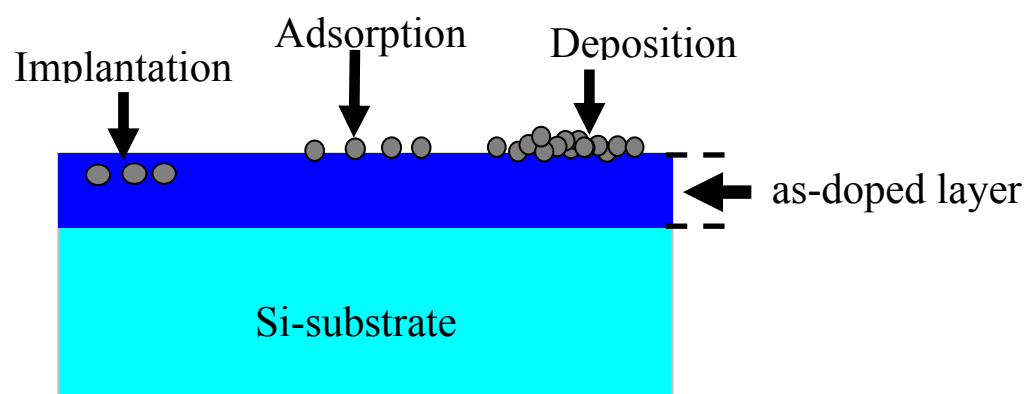
1.4-(i)Ultra-shallow junction Technology by plasma doping method

PD method which can be given low ion energy due to controlling bias energy is attracted because conventional beam line ion implantation method is too difficult to control low acceleration voltage.

The motivation of this particular study is as follows. Possible states of dopant materials introduced by plasma doping can be categorized as shown in this figure. In brief, most impurity atoms are implanted in the substrate, but significant amount of impurity atoms is adsorbed or deposited on the substrate surface. Boron atoms, however, are placed in very shallow surface region of the substrate in any case. Therefore, the doped layer can be susceptible to post cleaning treatment. This means that it is very important to establish an appropriate post cleaning process in order to control the resulting dose of the impurities.

Thus we decided to establish the post cleaning process for plasma doping. For this purpose, the effect of wet cleaning treatment was investigated in terms of retained dose variation depending on the use of different cleaning treatments.

Chapter2

Fabrication and Characterization Methods

2.1.1 Rapid thermal annealing (RTA)

Annealing process is needed one of the most important processes because of removing trap electrical charge into oxide films and recovering mobility and parameters of the other material due to activating ion after doping.

In this study, RTA (Rapid Thermal Annealing; MILA-3000) as shown in Fig.2.3 is used to anneal samples that is plasma doped Si wafers to activated completely doped impurities.

This RTA system has a heating method which fixes a lamp of infrared light to spot of a parabolic refractor of and then is reflected an infrared light in parallel.

The furnace temperature can be raised from Room Temperature (R.T.) to 1200 ^{o}C. Rate of temperature increase is same value or less than 50 ^{o}C/sec. Annealing is carried out in N_2 or O_2 ambient by running gas into furnace at atmospheric pressure. This system cannot be vacuumed and so completely be replaced by the gases.

Annealing condition were 1100   900°C for 3minutes or 10sec in N_2 or O_2 ambient.

In this work we study on Effects of surface treatment on retained dose of impurities doped by plasma doping. By using such a high temperature and long time annealing,) the total dose of B can be reliably estimated from the sheet resistances because the activation rate of the dopant atoms should be extremely high in this condition. The dose variation due to each wet treatment was then evaluated ad the results were normalized by comparing with the non treated case
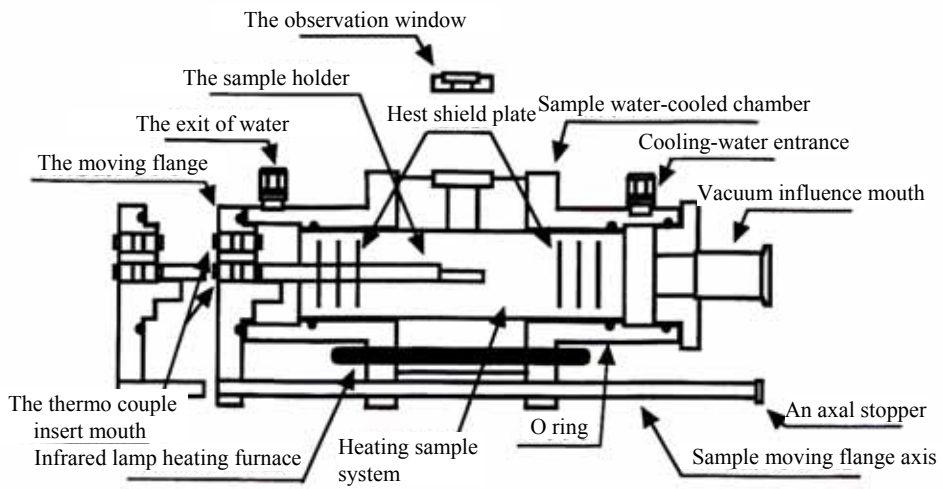
Fig. 2.3 (a) Photo and (b) The schematic overview
of RTA (MILA-3000) system

2.1.2 Plasma doping system

In Plasma doping, the intermediate stages of ion source, beam extraction, focusing, and scanning are omitted. The target is immersed in a plasma environment, and ions are extracted directly from the plasma and accelerated into the target by means of a series of negative high-voltage pulses applied to the target. Figure 2.6 and Fig.2.7 shows schematic and Photograph of Plasma Doping System, respectively used in this work. There are two chambers, such as loading and process chamber, two rf-power supplies (13.56MHz).This system has characteristic of low-pressure and high-density plasma source by helicon source. Helicon source has characteristics that a weak (50-200G) dc axial magnetic field together with an rf-driven antenna placed around of a helicon wave within the source plasma, and then resonant wave-particle interaction is believed to transfer the wave energy to the plasma. In addition to high-density and low-pressure, a feature is that the rf-power is coupled to the plasma across a dielectric window, rather than by direct connection to an electrode in the plasma, as for an rf-diode. When a sudden negative voltage $-V_0$ is applied to the target, then, leaving behind a uniform-density ion matrix. In pressure in loading chamber is about 10^{-2} Pa by a rotary pump connected to a turbo molecular pump. The background pressure in process chamber is about 10^{-5} Pa or less by a turbo molecular pump. During doping, the pressure is 0.1 to 2.5 Pa.In the process chamber, Argon (Ar) or Neon(Ne), Helium (He), and di-borane (B_2H_6) gases are introduced and is discharged by source power supply. And then target ion fed into the reactor and the plasma is generated by RF discharge. Plasma ions containing boron are then irradiated onto the wafer that is electrically biased by a separate power supply connected electrode under wafer holder.
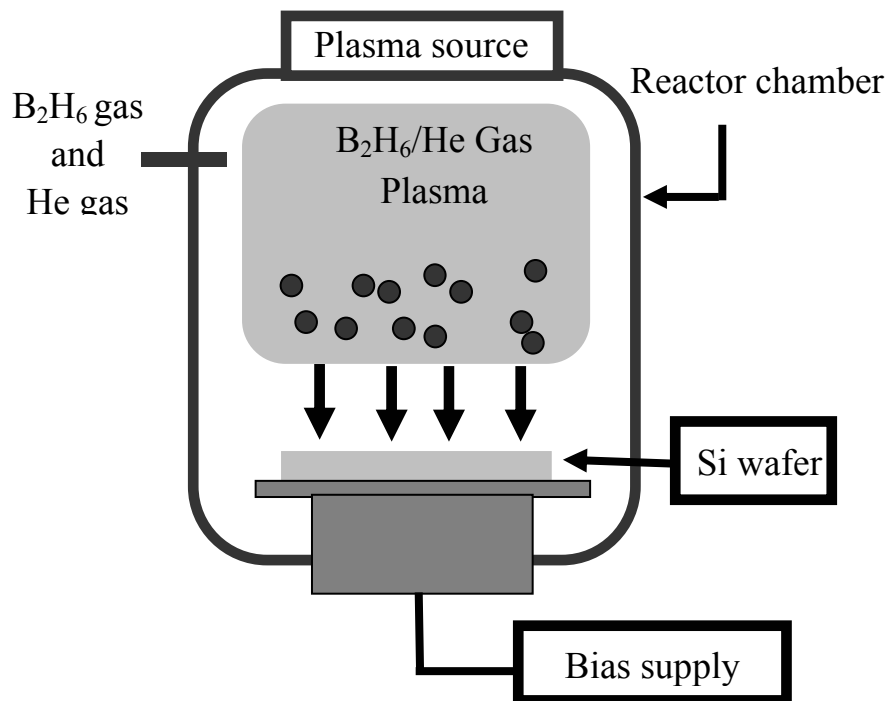
Fig.2.6 Cross section of Plasma Doping equipment. Plasma source, reactive chamber and wafer handling system are installed.

Plasma source

Reactor chamber

B_2H_6 gas
and
He gas

B_2H_6/He Gas
Plasma

Si wafer

Bias supply

Fig.2.7-i Photo of Plasma Doping system

Fig.2.7-ii Photo of Load Lock system

2.2.1 Atomic Force Microscopy (AFM)

Fig   shows Schematic of Atomic Force Microscopy (AFM). Micro probe forms itself into triangle and made of Si or Si3N4.

AFM has two measurement mode , one mode is contact-mode, the other mode is tapping mode.

When the back of micro probe are irradiated, the atomic force is worked by bringing it closed surface of samples in the back of   icro probe are irradiated. The change of material bending is detected reflected samples by 4 divided diode and

The surface roughness of the film is evaluated by Atomic force microscopy (AFM, Nano Scope 3, Digital Instrument Co. Ltd.) in tapping mode.

Figure2.9 shows principle of tapping mode AFM.   Tapping mode AFM accelerates cantilever with probe at the tip near resonant frequency, and so scan surface of the film tapping lightly intermittently.   The distortion is detected by a variation of reflection angle of laser beam which is irradiated to the cantilever.   The distance is controlled to keep the distortion constant while scanning in x and y directions and the control of the distance in z direction.

Spatial resolution of AFM used in this study is around 1.0 nm .

Boron atoms are placed in very shallow surface region of the substrate in any case. Therefore, the doped layer can be susceptible to post cleaning treatment. The purpose of this measurement is to measure roughness formed by plasma doping method or post surface treatment .
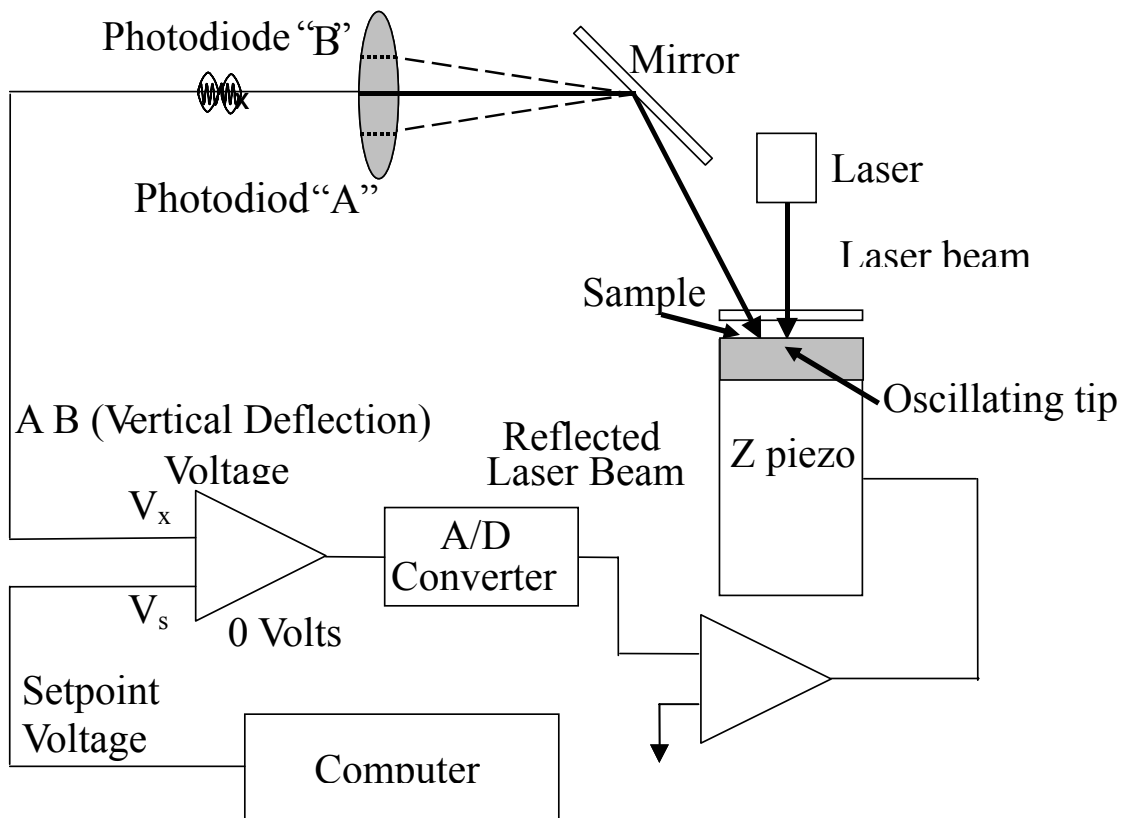
Figure.2.8-i Schematic of AFM
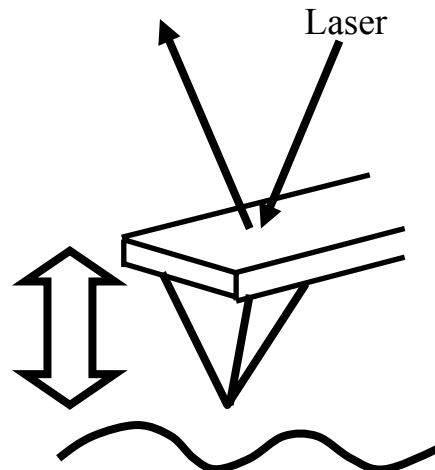

Figure. 2.8-(iii) Photo of AFM

Fig 2.8-(ii) Close up of micro probe. Material bending is detected by micro probe .

2.2.2 X-ray Photoelectron Spectroscopy (XPS)

Chemical state of a few nm surface layers is analyzed by X-ray Photoelectron Spectroscopy (XPS) as shown in Fig.2.10.   An electron is emitted by the photoelectric effect when homogeneous light is applied material.   The measuring method of electron energy and intensity distribution is called XPS method.

$$E_{kin}{}^{v} = hv - E_b - \phi$$

where $E_{kin}{}^{v}$, hv, E_b and ϕ are kinetic energy of liberated photoelectron, incident X-ray energy, binding energy of emitted electron for sample and work function for sample. If hv is constant, binding energy can be obtain by measuring the kinetic energy of emitted electron.   Identification of element is easily possible by measuring E_{kin} because binding energy of each electron orbit is different.   On the other hand, binding energy of same orbit of same element is changed a little by an atomic surrounding state and environment.   State analysis of element is possible by measuring this change variation called chemical shift.

Additionally, mean free path of electron is not so long because of scattering and absorption process of electron in solid.   Therefore, since XPS method can observe only the surface of nm order, it is suitable for thin film evaluation.
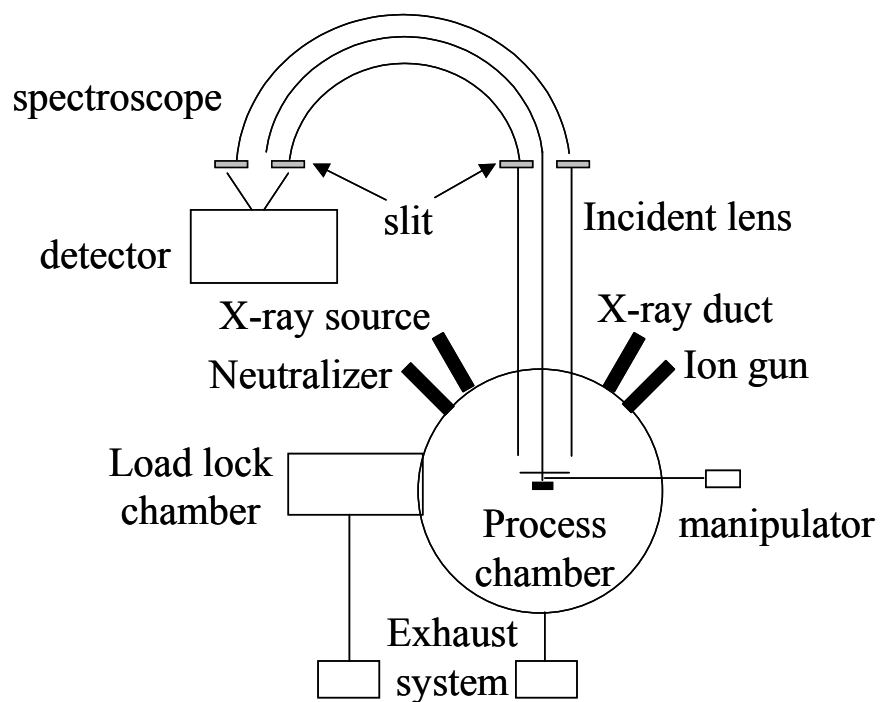
Fig.2.9 Schematic of XPS system

2.2.3 Spring-8

Synchrotron radiation is extremely powerful light which is used for studying the structure of matter at the atomic and electronic levels and in various physical and chemical processes in a number of research fields ranging from materials science to life science.

SPring-8, which is the largest third-generation synchrotron radiation facility in the world, provides the most powerful synchrotron radiation currently available.

At SPring-8, many researchers from around the world are making efforts to unlock the secrets of nature using synchrotron radiation as the key. Fig?? shows SPring-8 Storage Ring Parameters incident energy were 714eV.

used in this samples.

Synchrotron radiation (SR) is emitted from an electron traveling at almost the speed of light when its path is bent by a magnetic field. As it was first observed in a synchrotron in 1947, it was named "synchrotron radiation".

Ultra-bright

Highly directional

Spectrally continuos (BM/W) or quasi-monochromatic (U)

Linearly or circularly polarized

Pulsed with controlled intervals

Temporally and spatially stable

SPring-8 produces light that is about one billion times more brilliant than conventional X-ray sources.

Electron energy	8 GeV	Characteristic photon energy	28.9 keV
Current	100 mA	Number of insertion devices	Max 38
Circumference	1,436 m	Number of beamlines	Max 62

Figure 2.10-(i) SPring-8 Storage Ring Parameters
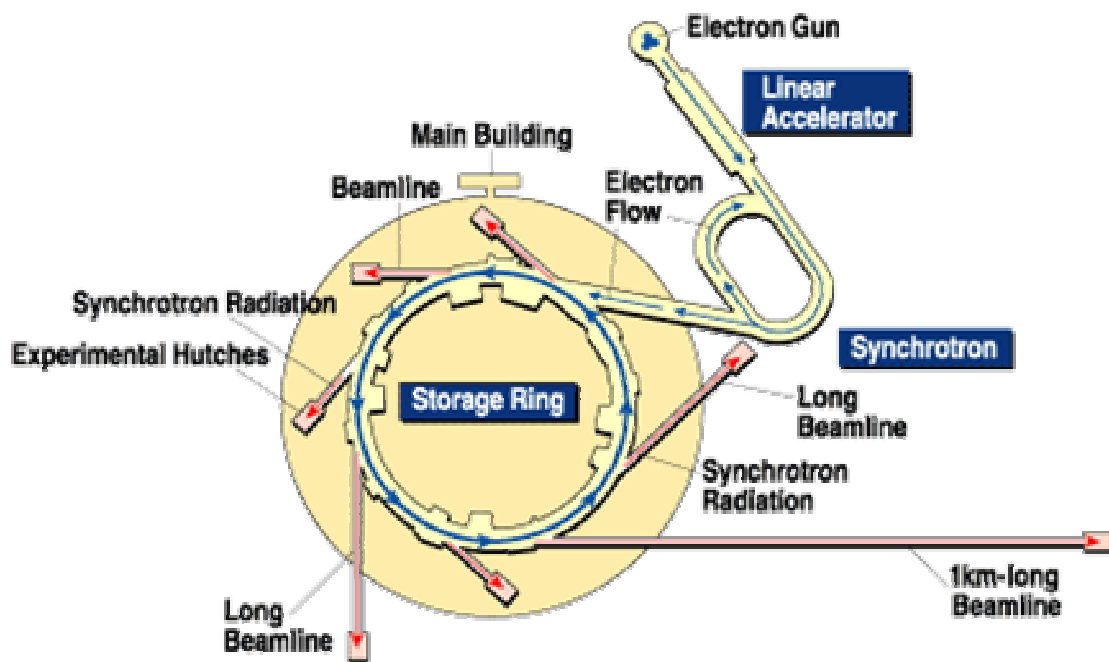
**Figure 2.10-(ii) Schematic of SPring-8**

2.2.4 Secondary Ion Mass Spectrometry (SIMS)

Depth profile, composition analysis of element and surface analysis of the sample is evaluated by Secondary Ion Mass Spectrometry (SIMS) as shown in Fig. This technique is element specific and is capable of detecting all elements as well as isotopes and molecular species. The basis of SIMS, shown in Fig.2.12, is the destructive removal of material from the sample by sputtering and the analysis of that material by a mass spectrometer. A primary ion beam (Ar^+, O_2^+, Cs^+ and etc.) impinges on the sample, and atoms from the sample are sputtered or ejected from sample.

Measurement by SIMS is explained in more detail under tri-level as follows;

(1)   A primary ion beam with 200 eV~20 keV is irradiated to a solid sample, and secondary ion and neutral particle are emitted from surface monolayers of a sample by sputtering phenomenon with an electron, X-rays and reflective ion.

(2)   Mass of positive or negative secondary ion is separated.

(3)   An elemental analysis for 2-dimention or 3-dimention of a sample is carried out by measuring intensity due to correcting separated secondary ion or by observing image.

Electronegative oxygen (O_2^+) is a secondary ion yield-enhancing species for electropositive elements (e.g., B and Al in Si) which produce predominantly positive secondary ions. The situation is reversed for electronegative elements (e.g., P, As and Sb in Si), having greater yields when sputtered with electropositive ions like cesium (Cs^+).

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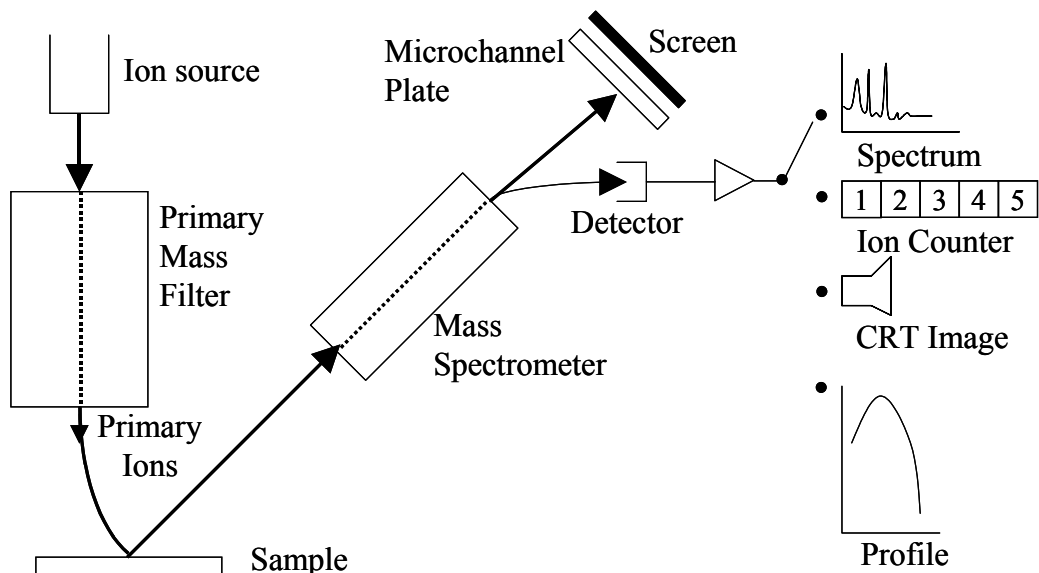
Figure.2.11 Schematic of SIMS system

2.2.5 Four-Point Probe

The four-point probe technique using four-probe is one of the most common methods for measuring the semiconductor resistivity because two-point probe methods are more difficult to interpret. This technique is calculated resistance by applying the current between outside 2 terminals (between A probe and D probe) and by measuring potential difference between inside 2 terminals (between B probe and C probe) as shown in Fig.2.13 The resistance by two-probe technique is higher than accurate resistance by including the contact resistance (R_c) at metal probe/semiconductor contact and spreading resistance (R_{sp}) under each probe. Nether R_c nor R_{sp} can be accurately calculated so that semiconductor resistance (R_s) cannot be accurately extracted from the measured resistance. On the other hands, four-probe technique can be neglected those parasitic resistances because the current value which flows between terminals is very small, and so potential drop can be disregarded. In this study, sheet resistance is measured by four-probe technique.

For an arbitrarily shaped sample the sheet resistance (ρ_{sh}) is given by

$$\rho_{sh} = \frac{V}{I} \times CF$$

where CF is correction factor that depends on the sample geometry. If distance between probes (s; in this study, s=1 mm) is very shorter than width of a sample (d), CF equals to $\pi/\ln(2)$=4.54.
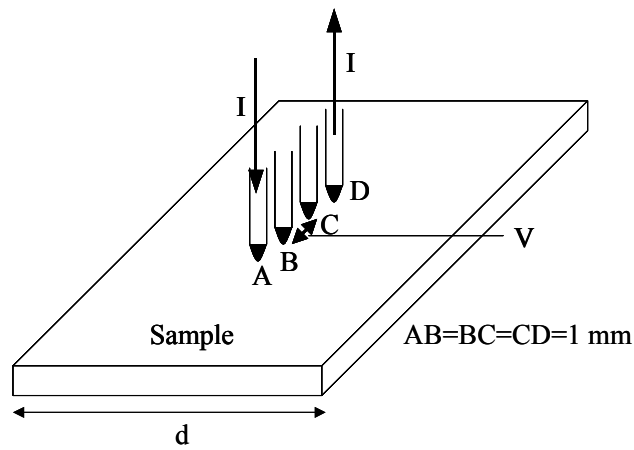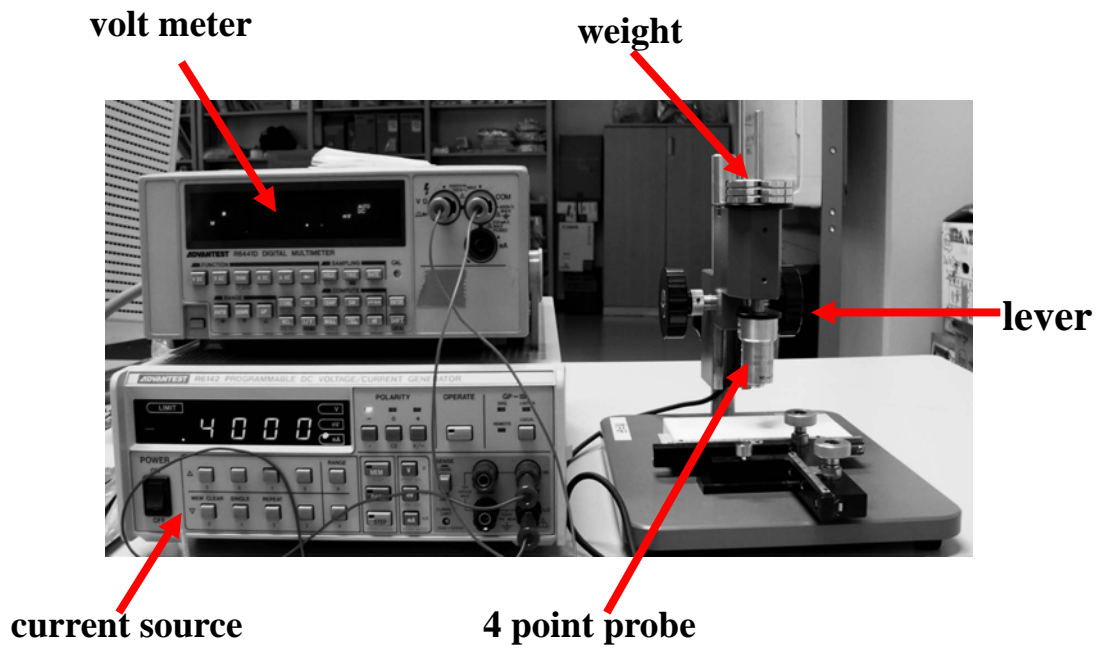
Figure.2.12 A collinear four-point probe

Figure 2.13 Photo of four point probe system

2.2.6 Spectro Ellipsometry (SE)

Ellipsometry as shown in Fig.2.14 is used predominantly to measure the thickness of thin dielectric films on highly absorbing substrates but can also be used to determine the optical constants of films or substrates by measuring the state of polarization of polarized light.   When light is irradiated at a material, the state of polarization is different from incident light and reflected light.   The state of reflected surface is measured by that difference.

The incident polarized light can be resolved into a component p, parallel to the plane of incidence and a component s perpendicular to the plane of incidence.   The two components experience different amplitudes and phase shifts upon reflection from absorbing materials and for multiple reflections in a thin layer between air and the substrate.   The complex reflection ratio   defined in terms of the reflection coefficients R_p and R_s or the ellipsometric angles . and

$$\rho = \frac{R_p}{R_s} = \tan(\Psi)^{j\Delta}$$

is measurable.

Ψ and Δ determine the differential changes in amplitude and phase, respectively, experience upon reflection by the component vibrations of the electric field vectors parallel and perpendicular to the plane of incidence.   Since Ψ and Δ are function of complex index of reflection, film thickness, incident angle and measured wavelength, film thickness can be calculated from the results of ellipso parameter.
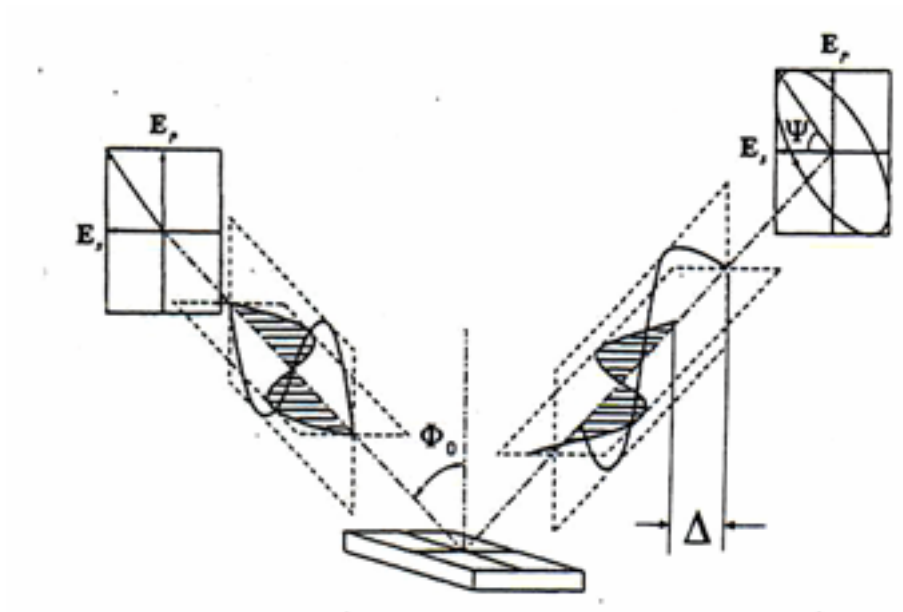
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Figure.2.14 Spectro Ellipsometry schematic

2.2.7 RCA wet cleaning (surface treatment)

RCA wet cleaning is the common cleaning process in Si surface cleaning. This cleaning In device processes Si wafer surface are acquired on several contamination. So These contaminations are removed by wet cleaning or surface treatment in order to remove them. Fig shows state of contamination such as carbonaceous organic matter (hydro carbon) particle metal ion and so on.

The basic matters of these contaminations to remove are as follows

Particles

Alkali metals (Na, K etc.) and / or Heavy metals

Carbonaceous organic matter

Si native oxide

It is suitable for RCA wet cleaning process to remove these contaminations. The mechanism of cleaning treatment is fond Fig as follows.

Dissolution from Si surface

Lift off from Si surface

Etching and prevention of reattachment

The purpose of use this process in my study is to establish the post cleaning process for plasma doping and the effect of wet cleaning treatment was investigated in terms of retained dose variation depending on the use of different cleaning chemicals.
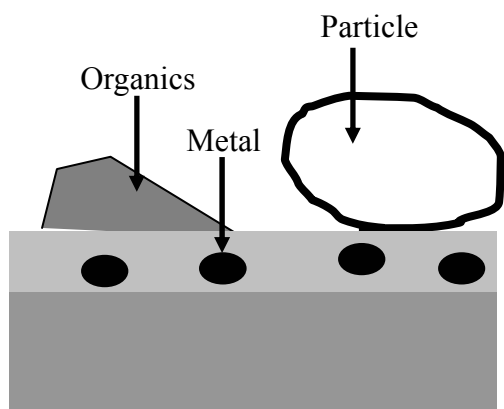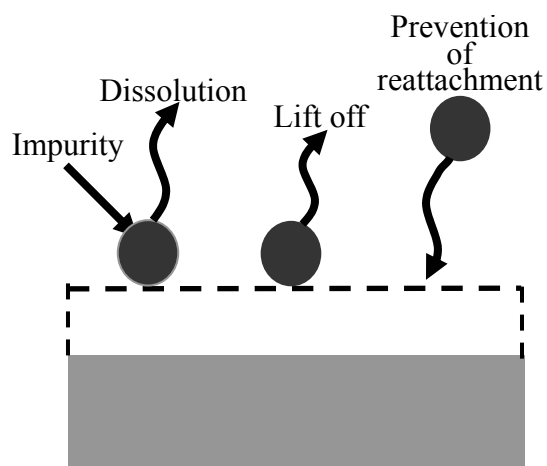
Figure 2.15state of
contamination on Si wafer

Figure 2.16 Mechanism
of cleaning treatment

Figure 2.17　Typical wet cleaning treatment for semiconductor process

name	Typical condition	Application	pH	Formation of oxide layer
APM (Ammonia hydroxide /hydrogen Peroxide Mixture)	NH4OH : H2O2 : H2O =1:1:5 or 0.05:1:5 (Volume ratio) 70　90 oC	Particle Organic	10　12	Generated
HPM (Hydrochloride /Hydrogen Peroxide Mixture)	HCl : H2O2 : H2O =1:1:5 (Volume ratio) 70　80oC	Metals	0　2	Generated
SPM (Sulfuricacid /hydrogen Peroxide Mixture)	H2SO4 : H2O2 =4:1 (Volume ratio) 80　120oC	Particle Metals	0　2	Generated
Hydrofluoric acid (HF)	HF Density: 0.5　1%	Si /native oxide	0　2	Removed

Chapter 3

Effects of surface treatments
on
the retained dose of
impurities
for
plasma doping

3.1 Experiment

Figure 2 shows experimental procedures employed in this work. Boron was doped by plasma doping method to n-type Si(100) wafers were used. When we did Plasma Doping on Si wafer surface , On the side of Load Lock we must operate carefully.

Figure ? shows the detail of the experimental conditions. In the initial plasma doping step, we employed the two doping conditions, one called "implantation dominant mode" and another called "deposition dominant mode". Between these two modes, various parameters such as source power, B_2H_6 gas concentration, wafer bias, doping time, and total gas pressure were difference. Principal of parameter used in this work is as follows. In the case of "implantation dominant mode" , source power was 1500W and in the case of "deposition dominant mode" , source power was 1000W . In the case of "implantation dominant mode" , Diborane (B_2H_6) gas concentration was 0.025-0.05% and in the case of "deposition dominant mode" , Diborane (B_2H_6) gas concentration was 5% . Bias voltage was plasma voltage (P.P.) to -200V, total gas pressure was 0.9-2.5 Pa, doping time (time of plasma discharge) was 30-90 seconds.

Roughly speaking, in the "implantation dominant mode", most boron ions are implanted in the substrate, whereas, in the "deposition dominant mode", the deposited boron dose on the surface is relatively high.

The table at the bottom shows the conditions of the wet treatment processes. HF treatment was performed by using 1%-diluted solution at RT, and, SPM and APM processes were performed at these concentrations and temperatures.

The table at the bottom shows the conditions of each wet treatment process we employed including HF, SPM and APM.

These as-doped wafers were treated with one of the wet cleaning processes or low temperature annealing O_2 ambient. ; 1%-diluted HF at room temperature, APM ($NH_4OH : H_2O_2 : H_2O = 1 : 1 : 5$) at 80^oC, or SPM ($H_2SO_4 : H_2O_2 = 4 : 1$) at 80^oC. After that, these samples were annealed at 1100^oC for 3minutes in N_2 ambient.

However these samples which surface treatment was done were annealed by Rapid Thermal annealing. The reason of such as fast time annealing was to return these data to the latest annealing process like a Flash Lamp Annealing and Spike annealing and Laser annealing method. Long time and very high tempreture annealing condition was employed by giving priority to complete electrical activation of boron in order to estimate boron dose from sheet resistance, rather than obtaining shallow junctions. The sheet resistance were measured by four-point probe method.

	Wafer Type	N	N
	Substrate resistance	8-12 ohms	8-12 ohms
	Gas	B2H6/He	B2H6/He
PD Condition	Gas ratio	0.05%/99.975%	5%/95%
	Source Pwer [W]	1500	1000
	BiasVdc [V]	0-100	60-100
	Pressure [Pa]	0.9	2.6
	Process Time [sec.]	30	60-90

Plasma doping with B_2H_6 / He
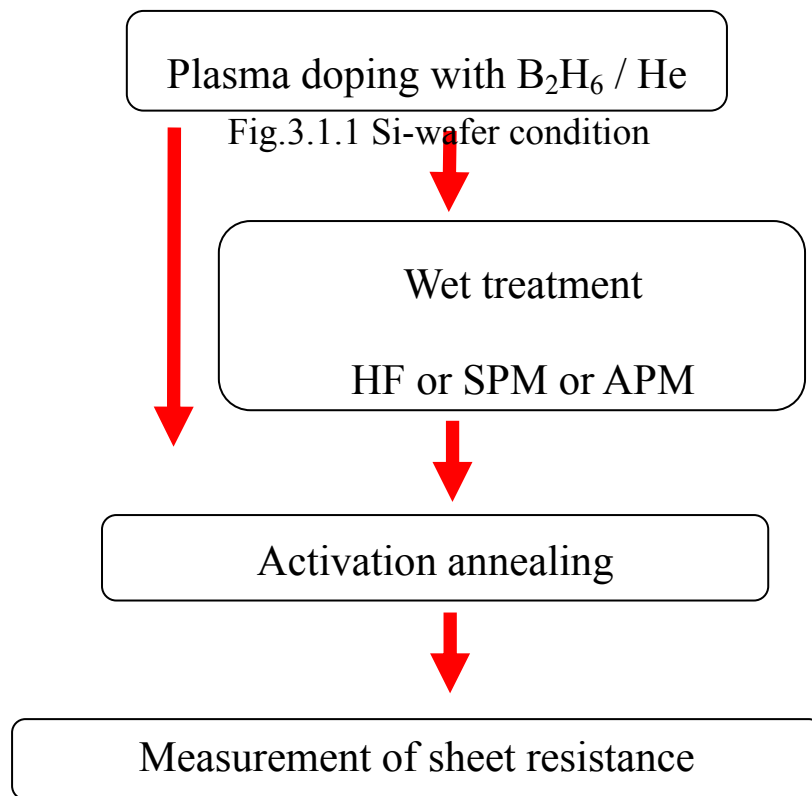
Fig.3.1.1 Si-wafer condition

Wet treatment

HF or SPM or APM

Activation annealing

Measurement of sheet resistance

Fig.3.1.2experimental procedures
for wet treatment

Wet treatment

Wet treatment
HF or SPM or APM

↓

Rinse1   (UPW)

↓

Rince2 (UPW)

Wet treatment

HF(1% at Room Temperature
SPM $H_2SO_4 : H_2O_2$ = 4 : 1 at 80 °C
APM $NH_4OH : H_2O_2 : H_2O$ = 1 : 1 : 5 at 80 °C
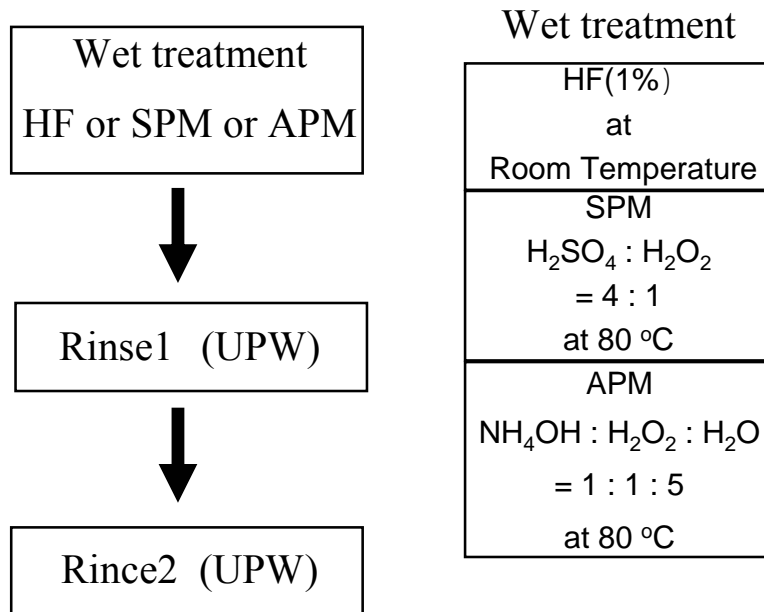
Fig.3.1.3 wet treatment procedures

Plasma doping with B_2H_6 / He

Thermal treatment O_2 ambient 500^oC 5-10min

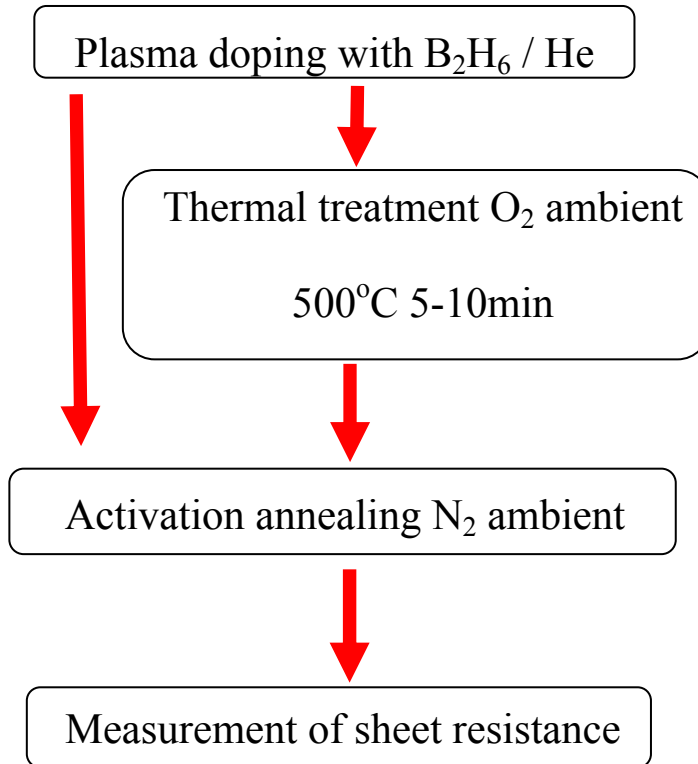| Activation annealing N_2 ambient |
|---|

Measurement of sheet resistance

Fig.3.1.2experimental procedures
for thermal treatment

3.2 Results

3.2.1 SIMS profile

Figure ?? shows SIMS profiles of boron for the samples prepared by the "implantation dominant mode". Profiles are found to be deeper with increase of bias voltage, however, doped layer depth is shallower than 15 nm even at bias of 200V. Boron concentrations at surfaces seem to be very high in all cases. It had been found that apparent deposition did not occur as far as process parameters employed in the "implantation dominant mode" were used and intentional bias voltage was applied. However, in the case of bias condition of P.P., the SIMS profile indicated possibility of some deposition on the Si surface.

The plasma doping condition was RF source power was 1000-1500W, gas concentration of B_2H_6 (He diluted) was 0.025-5.0%, bias voltage was plasma voltage (P.P.) to -200V, total gas pressure was 0.9-2.5 Pa, doping time (time of plasma discharge) was 30-90 seconds.

In the case of as-doped sample, sheet resistance was about 260 (ohm / sq) before compensation. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 5.5×10^{15} (cm^{-2}) observed by SIMS profile.

And at bias 200V of Plasma Doping condition In the case of zero min. of treatment time , sheet resistance was about 350 (ohm / sq) before compensation. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 3.8×10^{14} (cm^{-2}) at bias 200V of Plasma Doping condition..

In the case of zero min. of treatment time , sheet resistance was about 170 (ohm / sq) before compensation at bias Plasma Potential of Plasma Doping condition. When we

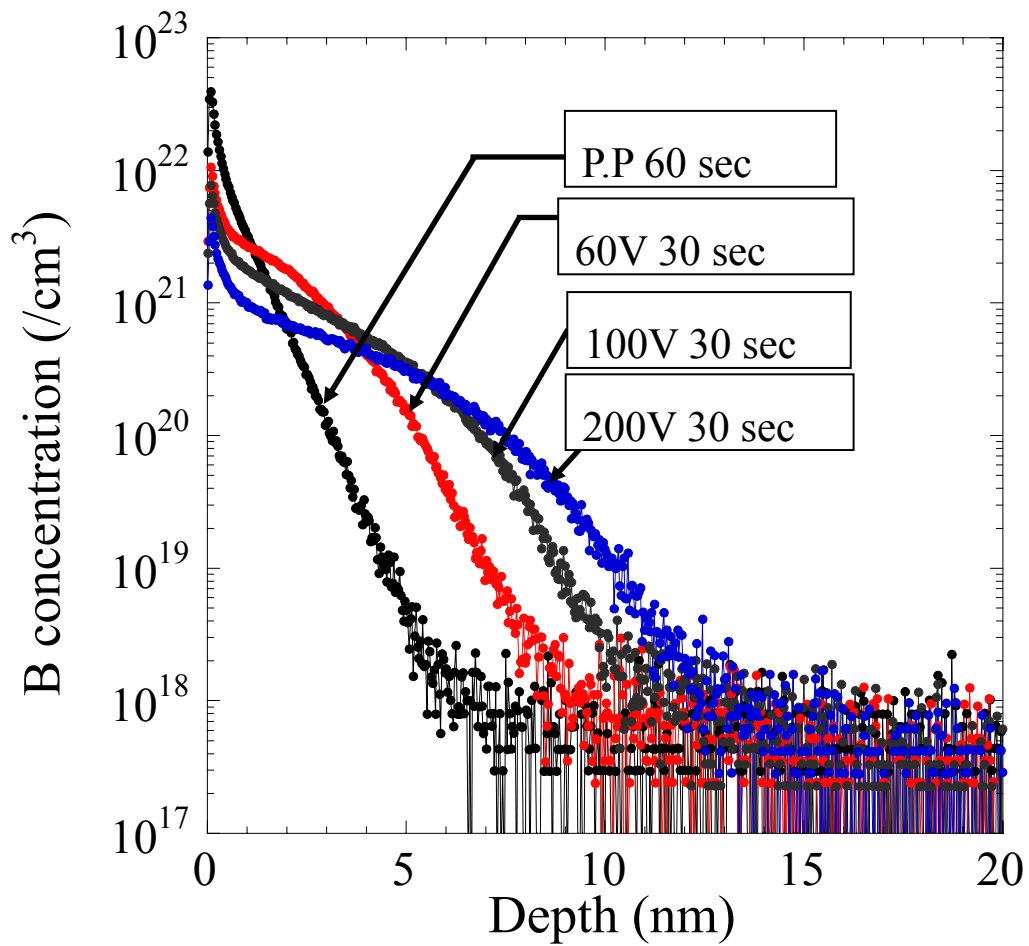evaluated dose of Boron from this sheet resistance , Dose of Boron was 1.2×10^{14} (cm^{-2}).

Fig.3.2.1 SIMS profiles of boron for as-doped sample

by "implantation dominant mode".

3.2.2 SPM treatment in the case of "implantation dominant mode"

This figure ?? shows the results of the dose variation by the SPM treatment as a function of time. The vertical axis was the boron dose normalized by the non-treated references and the horizontal axis was the treatment time. Zero min. of treatment time meant the non-treated condition and all the data were normalized at this point. The figure ??? was the results of Dose variation by post SPM treatment of the "implantation dominant mode" and the figure ??? was the results of the "deposition dominant mode".

Significant increase in dose due to the SPM treatment was observed. Comparing between the two doping modes, the dose increase was larger in the case of the "implantation dominant mode".

Firstly, as the result of the dose variation by post SPM treatment of "implantation dominant mode" was discussed here.

In the case of zero min. of treatment time , sheet resistance was about 350 (ohm / sq) before compensation. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 3.8×10^{14} (cm^{-2}). In the 5 min of the SPM treatment time the dose was 10 percent larger than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition .As the SPM treatment time was 10 minutes , the dose was about 30 percent larger than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . However Figure ??? was not shown about the case of 20 minutes. of treatment time, on bias 100V of Plasma Doping condition , the result of 20 minutes SPM treatment time was as large as 10 minutes.

In the case of zero min. of treatment time , sheet resistance was about 350 (ohm / sq)

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before compensation(wafer bias was 100V). When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 3.8×10^{14} (cm^{-2}). In the 5 min of the SPM treatment time the dose was 15 percent larger than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition .As the SPM treatment time was 10 minutes , the dose was about 30 percent larger than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . However Figure ??? was not shown about the case of 20 minutes. of treatment time, on bias 100V of Plasma Doping condition , the result of 20 minutes SPM treatment time was saturated and as large as 10 minutes.

  In the case of zero min. of treatment time , sheet resistance was about 220 (ohm / sq) before compensation(wafer bias was 60V).When the wafer bias was 60V, sheet resistance was smaller than bias condition 100V. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 8.5×10^{14} (cm^{-2}). In the 5 min of the SPM treatment time the dose was 5 percent larger than in the case of zero min. of treatment time, In bias 60V of Plasma Doping condition .As the SPM treatment time was 10 minutes , the dose was about 10 percent larger than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . the case of 20 minutes. of treatment time, on bias 60V of Plasma Doping condition , the result of 20 minutes SPM treatment time was saturated and as large as 10 minutes.
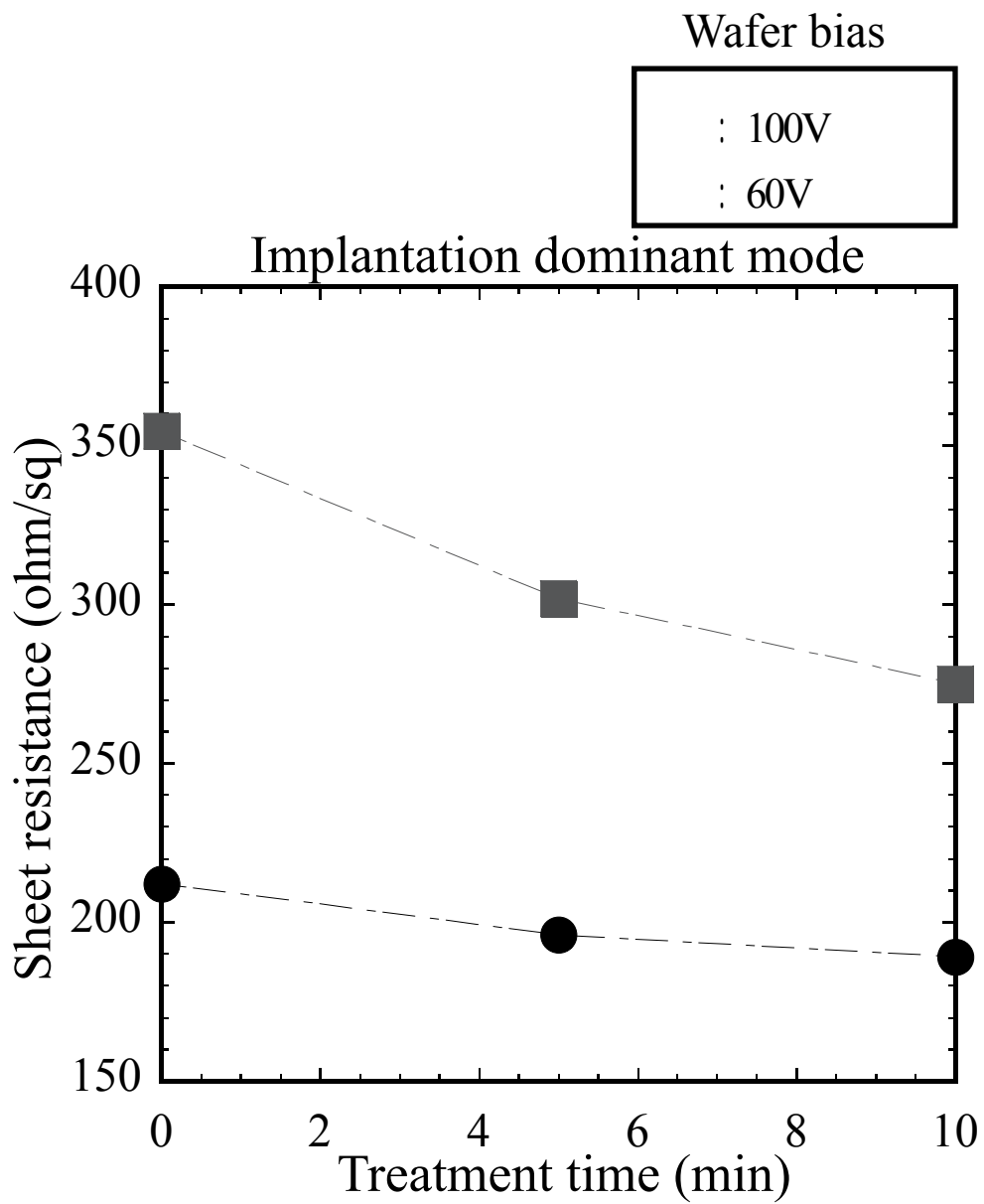
Fig.3.2.2 variation of sheet resistance by post

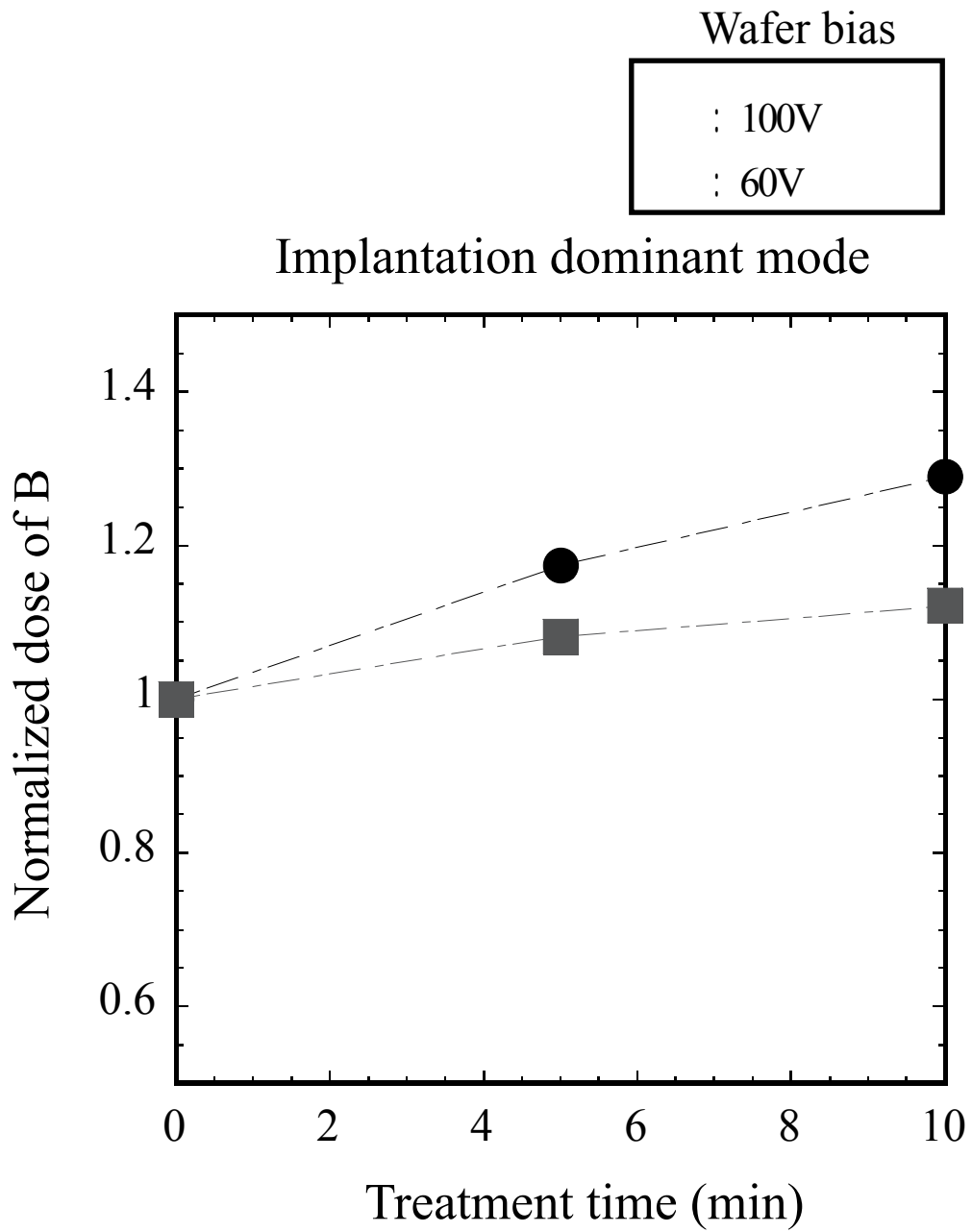SPM treatment . In case of implantation

Fig.3.2.3 Dose variation by post SPM

treatment . In case of implantation dominant

3.2.3 SPM treatment in the case of "deposition dominant mode"

Figure ?? shows variation of sheet resistance by post SPM treatment . And Figure ?? shows Dose variation by post SPM treatment . in case of deposition dominant mode. In case of deposition dominant Then the dose variation by post SPM treatment of "deposition dominant mode" was discussed. The vertical axis was the boron dose normalized by the non-treated references and the horizontal axis was the treatment time. Zero min. of treatment time meant the non-treated condition and all the data were normalized at this point. The figure ??? was the results of Dose variation by post SPM treatment of the figure ??? was the results of the "deposition dominant mode" .In the case of zero min. of treatment time , sheet resistance was about 73 (ohm / sq) before compensation(wafer bias was 60V).When the wafer bias was 60V, sheet resistance was smaller than bias condition 100V. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 4.5×10^{15} (cm^{-2}). In the 5 min of the SPM treatment time the dose was almost the same as large as in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . In the 10 min of the SPM treatment time the dose was 2percent smaller than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . In the 5 min of the SPM treatment time the dose was 10 percent larger than in the case of zero min. of treatment time, In bias 60V of Plasma Doping condition . In the 10 min of the SPM treatment time the dose was 10 percent larger than in the case of zero min. of treatment time, In bias 600V of Plasma Doping condition. Both case of treatment time in "deposition dominant mode", variation of Boron dose were almost the same value.
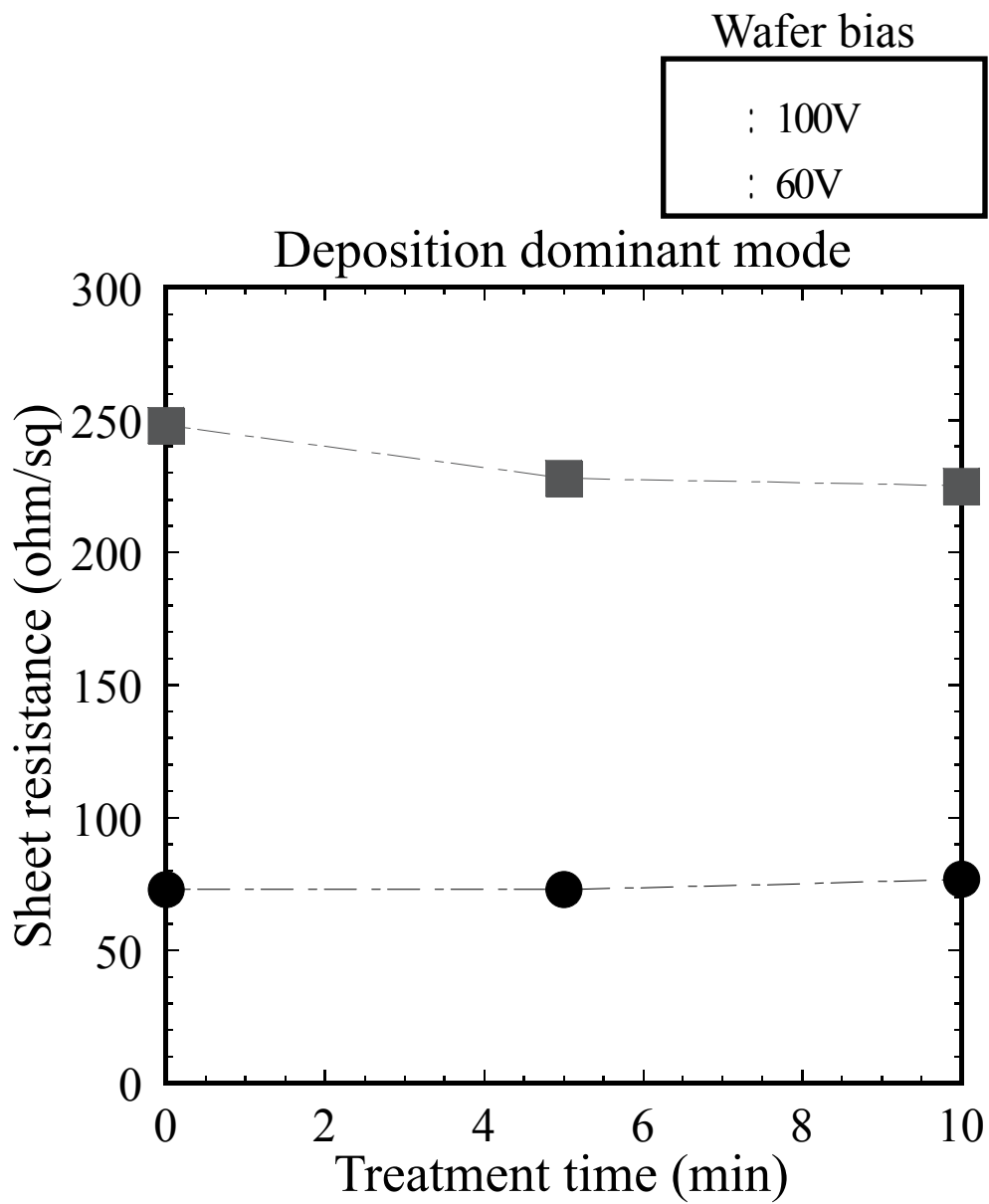
42

Fig.3.2.4variation of sheet resistance by post
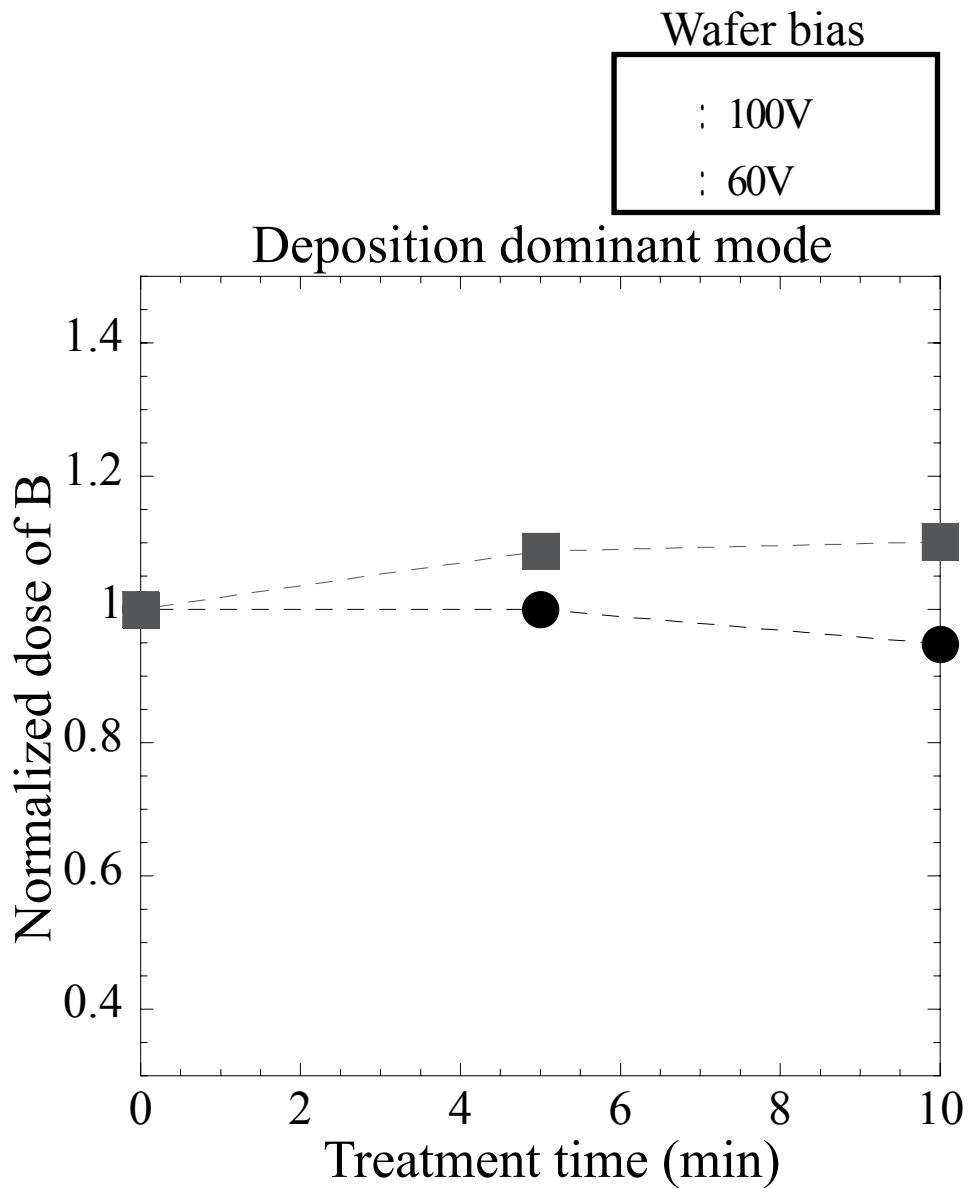
SPM treatment . In case of deposition

Fig.3.2.5 Dose variation by post SPM

treatment . In case of deposition dominant

3.2.4 HF treatment

This figure ?? showed the results of the dose variation by the HF treatment as a function of time. The vertical axis was the boron dose normalized by the non-treated references and the horizontal axis was the treatment time. Zero min. of treatment time meant the non-treated condition and all the data were normalized at this point. The figure ??? was the results of Dose variation by post HF treatment of the "implantation dominant mode" and the figure ??? was the results of the "deposition dominant mode".

Significant increase in dose due to the HF treatment was observed. Comparing between the two doping modes, the dose decrease was larger in the case of the "deposition dominant mode".

Contrary to the previous results by SPM, B dose largely decreased in this case.

As for the difference between the two doping modes, the decrease in dose was larger on the "deposition dominant mode"

Firstly, as the result of the dose variation by post SPM treatment of "implantation dominant mode" was discussed here.

In the case of zero min. of treatment time , sheet resistance was about 260 (ohm / sq) before compensation. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 5.5×10^{15} (cm^{-2}). In the 5 min of the HF treatment time the dose was 10 percent larger than in the case of zero min. of treatment time, In bias 200V of Plasma Doping condition In the case of zero min. of treatment time , sheet resistance was about 350 (ohm / sq) before compensation. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 3.8×10^{14} (cm^{-2}) at bias 200V of Plasma Doping condition.. In the case of zero min. of treatment time, sheet resistance was about 170

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(ohm / sq) before compensation at bias Plasma Potential of Plasma Doping condition. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 1.2 $\times 10^{14}$ (cm^{-2}).

In the 5 min of the HF treatment time the dose was 20 percent smaller than in the case of zero min. of treatment time, In bias 200V of Plasma Doping condition. As the HF treatment time was 10 minutes , the dose was about 40 percent larger than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . As the HF treatment time was 10 minutes , the dose was about 50 percent larger than in the case of zero min. of treatment time, In bias 200V of Plasma Doping condition .

However Figure ??? was not shown about the case of 20 minutes. of treatment time, on bias 100V of Plasma Doping condition , the result of 20 minutes HF treatment time was as large as 10 minutes.

In bias 100V of Plasma Doping condition .As the HF treatment time was 10 minutes , the dose was about 30 percent smaller than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . However Figure ??? was not shown about the case of 20 minutes. of treatment time, on bias 100V of Plasma Doping condition , the result of 20 minutes HF treatment time was saturated and as large as 10 minutes.
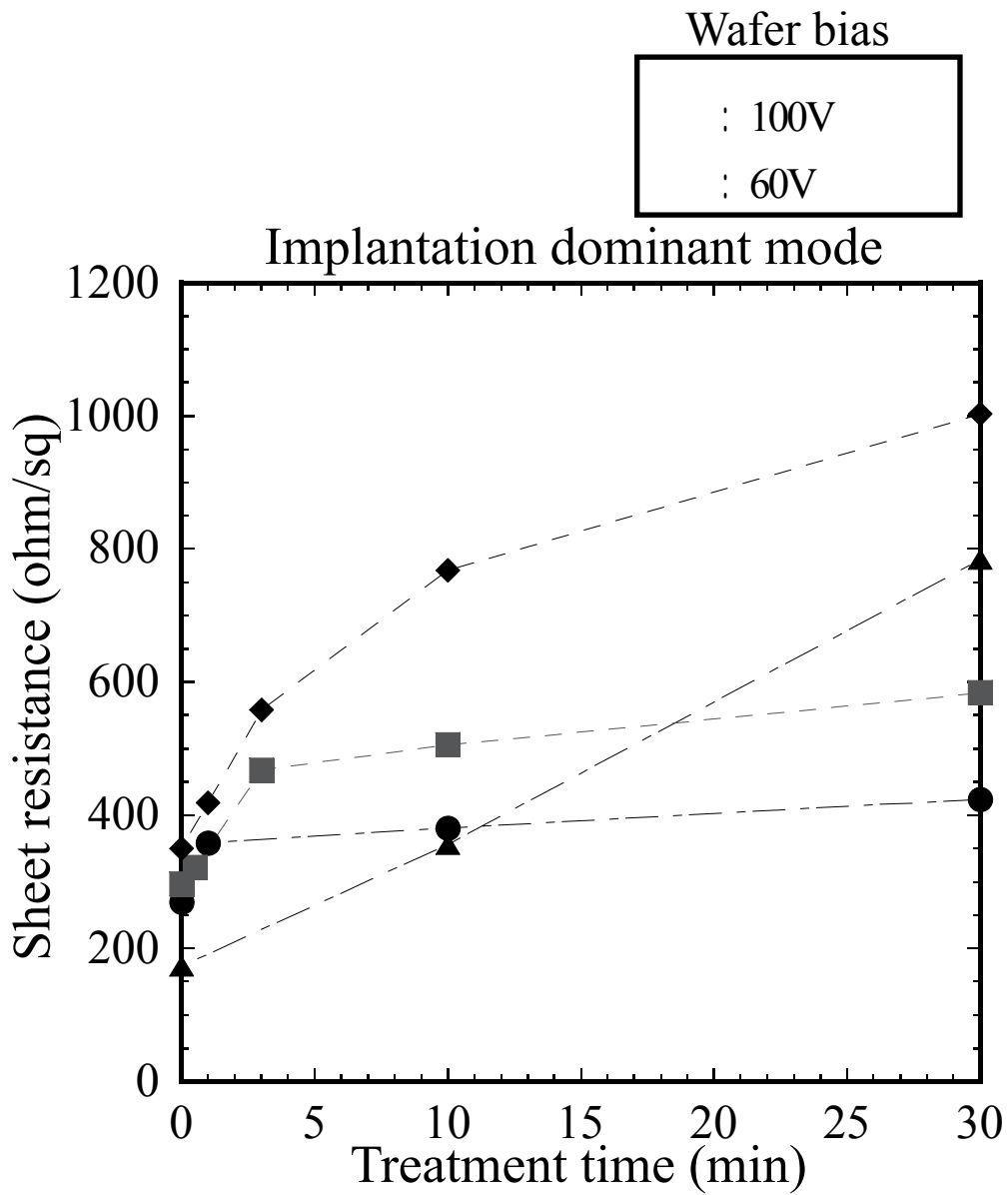
Fig.3.2.6 variation of sheet resistance by post

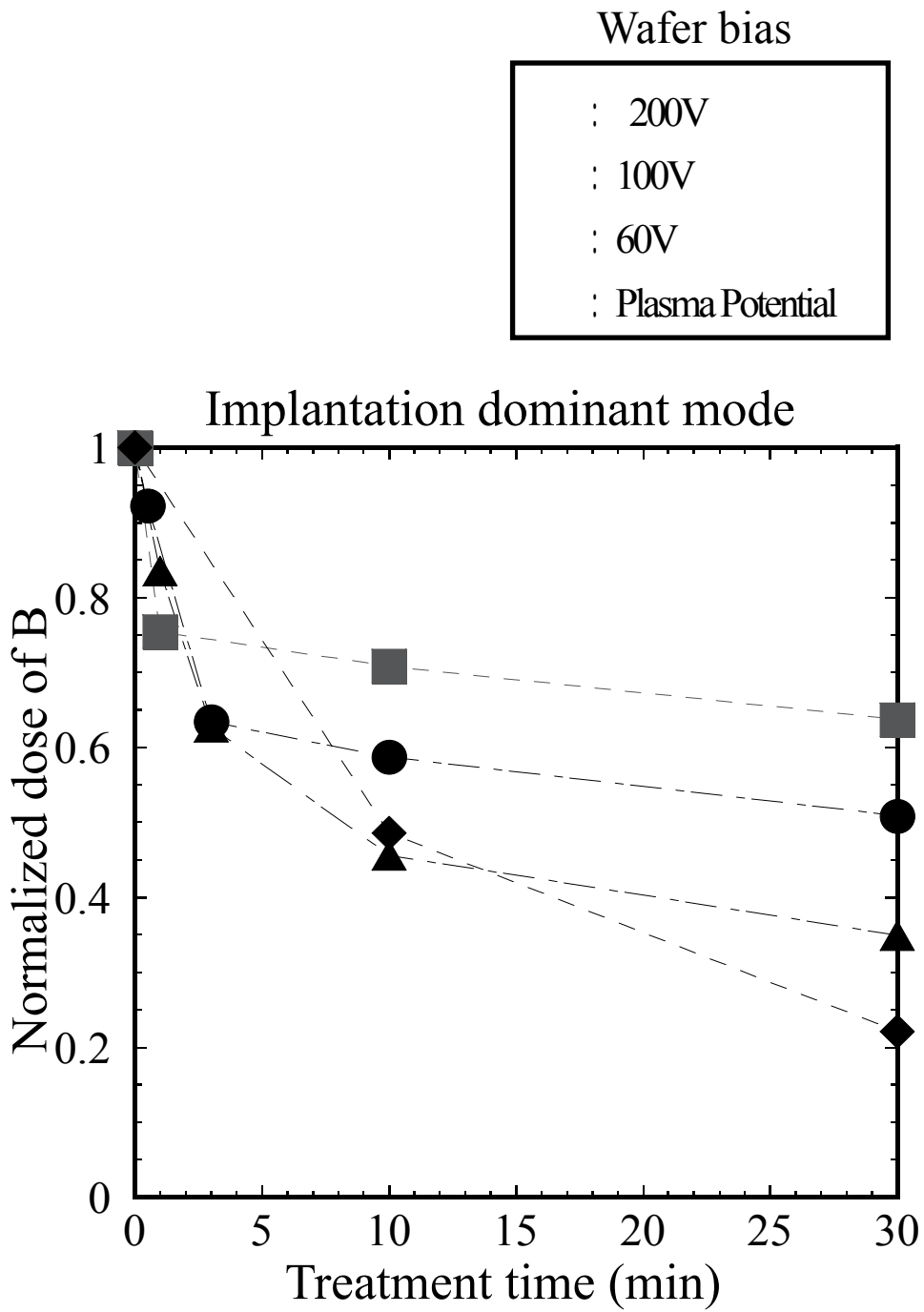SPM treatment . In case of implantation

Wafer bias

200V
100V
60V
Plasma Potential

Implantation dominant mode

Fig.3.2.7 Dose variation by post HF treatment .
implantation dominant mode

3.2.5 HF treatment in the case of "deposition dominant mode"

Then the dose variation by post HF treatment of "deposition dominant mode" was discussed. The vertical axis was the boron dose normalized by the non-treated references and the horizontal axis was the treatment time.   Zero min. of treatment time meant the non-treated condition and all the data were normalized at this point.   The figure ??? was the results of Dose variation by post HF treatment of the figure ??? was the results of the "deposition dominant mode" .In the case of zero min. of treatment time , sheet resistance was about 73 (ohm / sq) before compensation(wafer bias was 60V).When the wafer bias was 60V, sheet resistance was smaller than bias condition 100V. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 4.5×10^{15} (cm^{-2}). In the 5 min of the SPM treatment time the dose was almost the same as large as in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . In the 10 min of the HF treatment time the dose was 60percent smaller than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . In the 5 min of the HF treatment time the dose was 70 percent larger than in the case of zero min. of treatment time, In bias 60V of Plasma Doping condition . In the 10 min of the HF treatment time the dose was 10 percent larger than in the case of zero min. of treatment time, In bias 60V of Plasma Doping condition. Both case of treatment time in "deposition dominant mode", variation of Boron dose were larger than in the case of "implantation dominant mode".
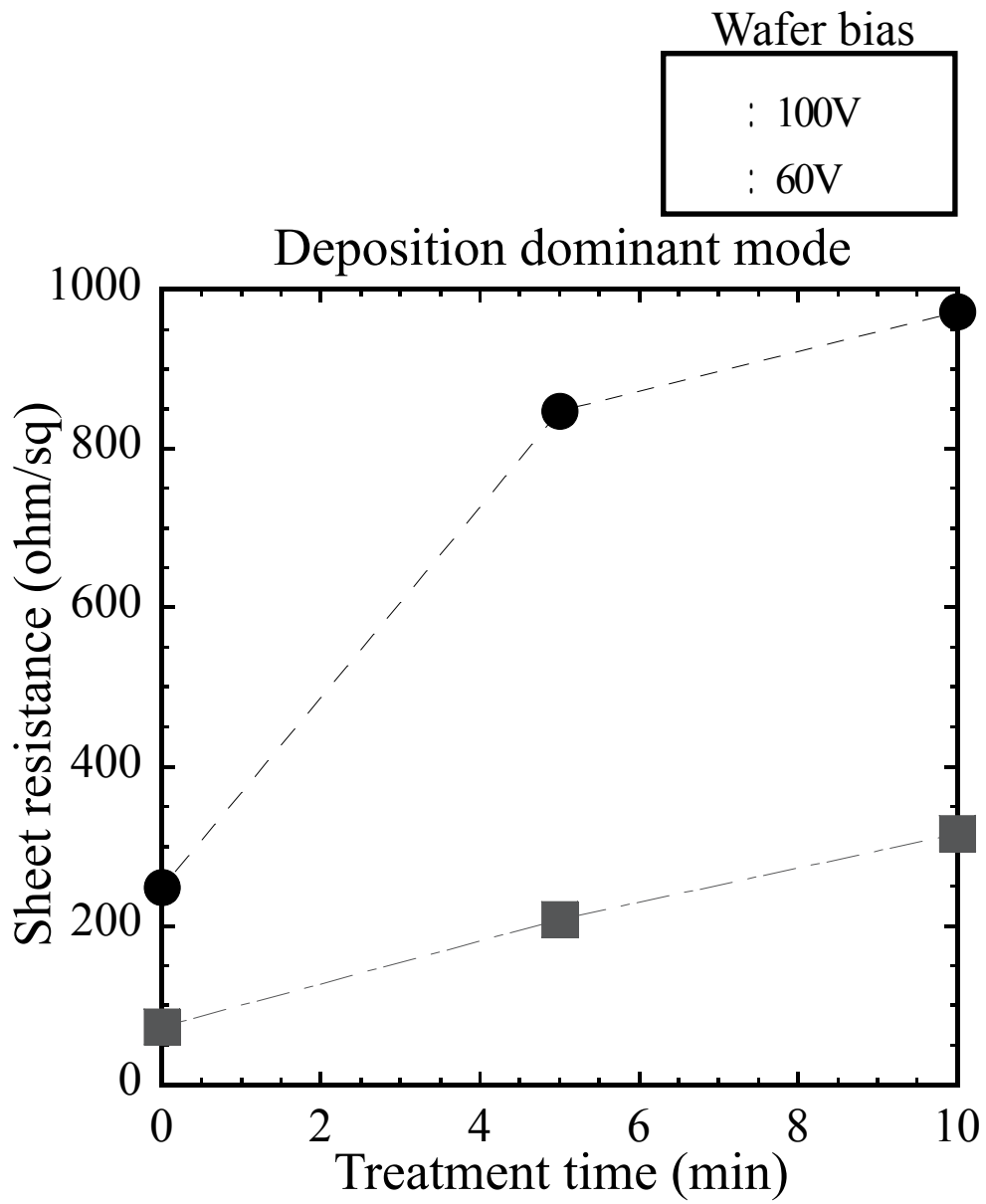
49

Fig.3.2.8 variation of sheet resistance by post
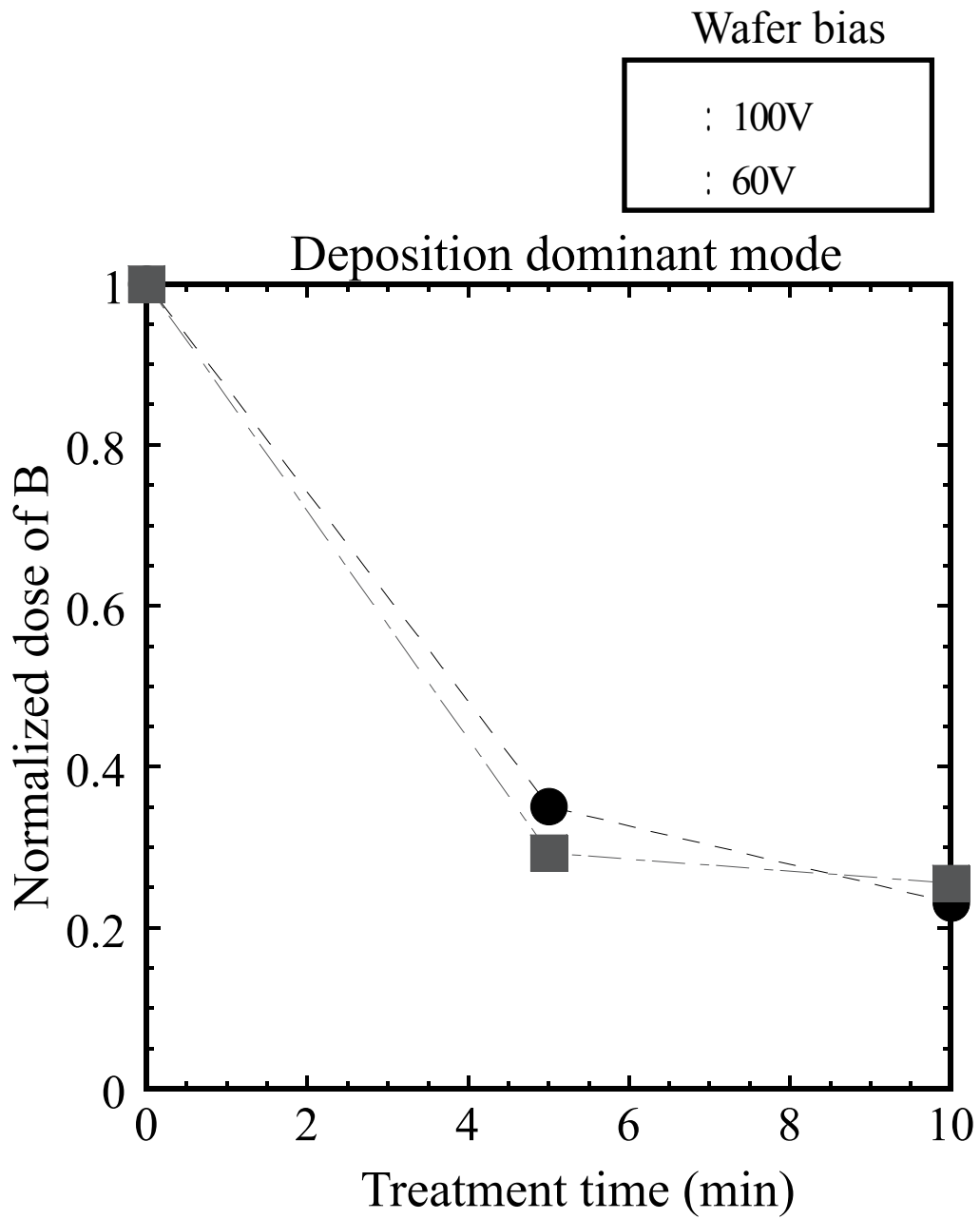
HF treatment . In case of deposition dominant

Fig.3.2.9 dose variation by post HF

treatment . In case of deposition dominant

3.2.6 APM treatment in the case of "implantation dominant mode"

This figure ?? showed the results of the dose variation by the APM treatment as a function of time.   The vertical axis was the boron dose normalized by the non-treated references and the horizontal axis was the treatment time.   Zero min. of treatment time meant the non-treated condition and all the data were normalized at this point.   The figure ??? was the results of Dose variation by post SPM treatment of the "implantation dominant mode"   and the figure ??? was the results of the "deposition dominant mode".

In this case, the dose decreased significantly but the change was smaller than that of the HF.   It should also be noted that the decrease in dose was larger on the "deposition dominant mode", which is similar to the case of the HF treatment.

Firstly, as the result of the dose variation by post APM treatment of "implantation dominant mode" was discussed here.

In the case of zero min. of treatment time , sheet resistance was about 220 (ohm / sq) before compensation. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 5.3×10^{15} (cm^{-2}). In the 5 min of the APM treatment time the dose was as large as in the case of zero min. of treatment time, in bias 100V of Plasma Doping condition .As the APM treatment time was 10 minutes , the dose was about 10 percent larger than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . However Figure ??? was not shown about the case of 20 minutes. of treatment time, on bias 100V of Plasma Doping condition , the result of 20 minutes SPM treatment time was as large as 10 minutes.

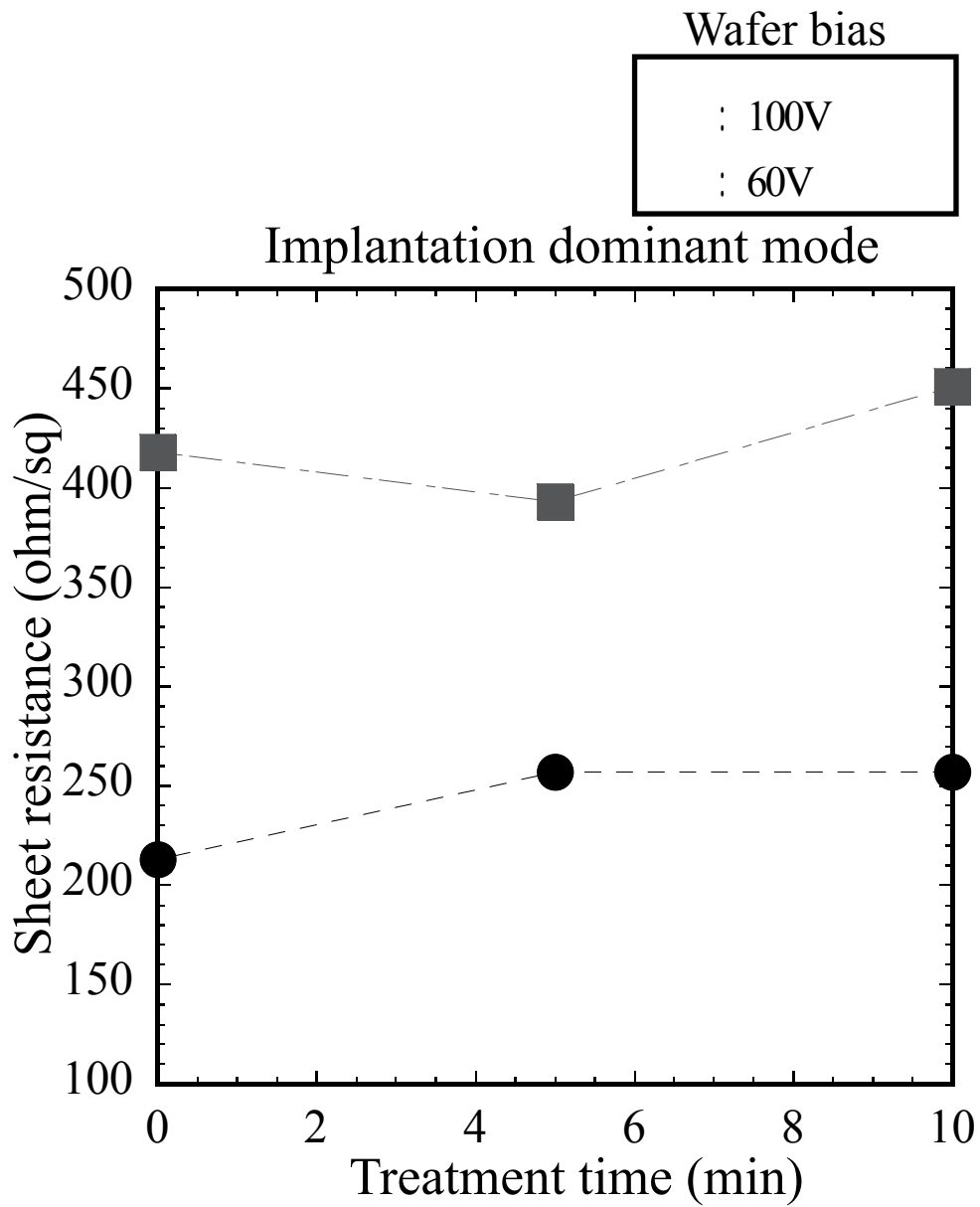In the case of zero min. of treatment time , sheet resistance was about 420 (ohm / sq) before compensation(wafer bias was 60V). When we evaluated dose of Boron from this

sheet resistance, Dose of Boron was 3.0 $\times 10^{14}$ (cm^{-2}). In the 5 min of the APM treatment time the dose was 15 percent larger than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition .As the APM treatment time was 10 minutes, the dose was about 30 percent larger than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . However Figure ??? was not shown about the case of 20 minutes. of treatment time, on bias 100V of Plasma Doping condition , the result of 20 minutes APM treatment time was saturated and as large as 10 minutes.

  In the case of zero min. of treatment time , sheet resistance was about 220 (ohm / sq) before compensation(wafer bias was 60V).When the wafer bias was 60V, sheet resistance was smaller than bias condition 100V. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 8.5 $\times 10^{14}$ (cm^{-2}). In the 5 min of the APM treatment time the dose was 5 percent larger than in the case of zero min. of treatment time, In bias 60V of Plasma Doping condition .As the APM treatment time was 10 minutes , the dose was about 10 percent larger than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . the case of 20 minutes. of treatment time, on bias 60V of Plasma Doping condition , the result of 20 minutes APM treatment time was saturated and as large as 10 minutes.
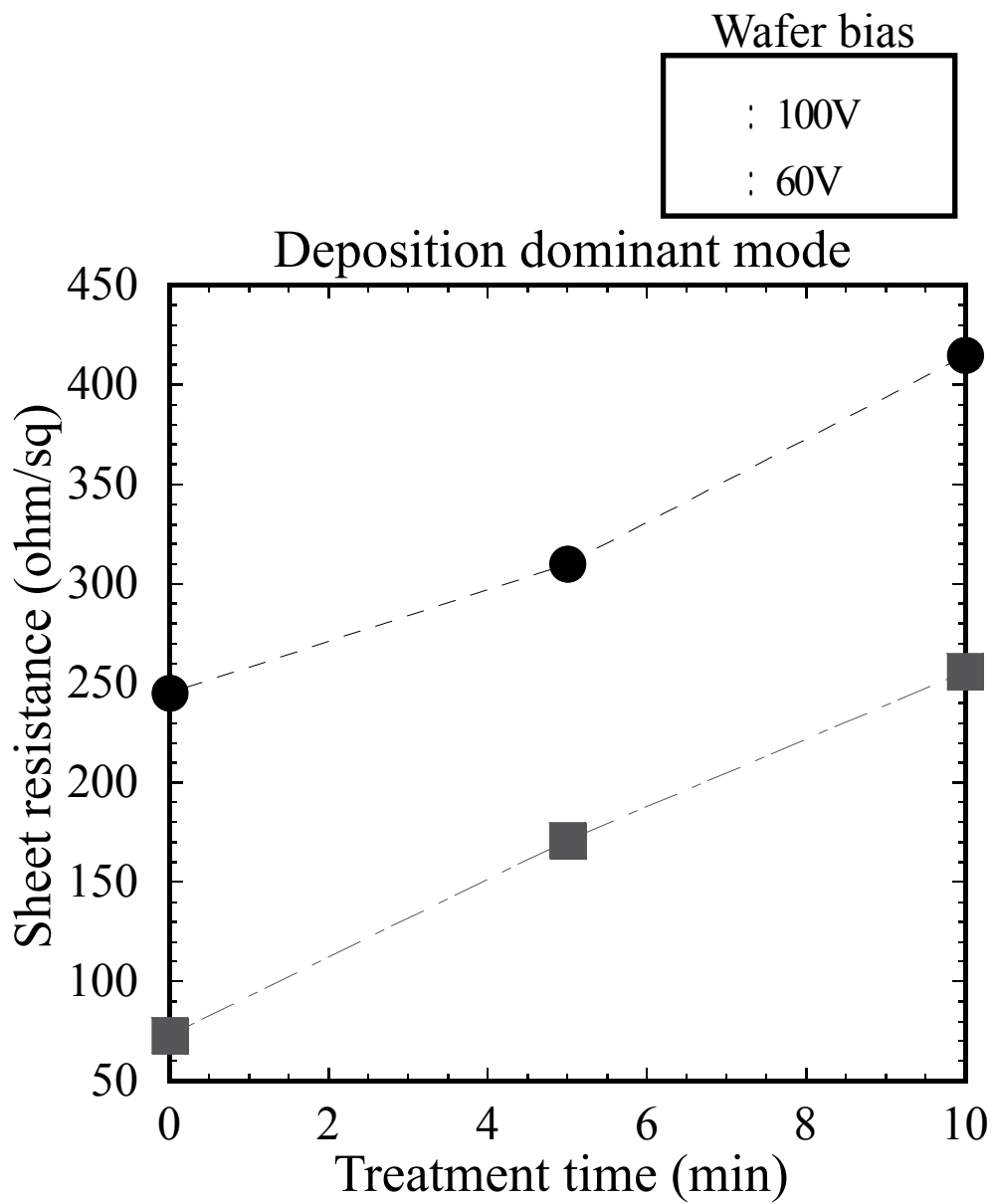
Fig.3.2.10 Variation of sheet resistance by post

APM treatment . In case of implantation
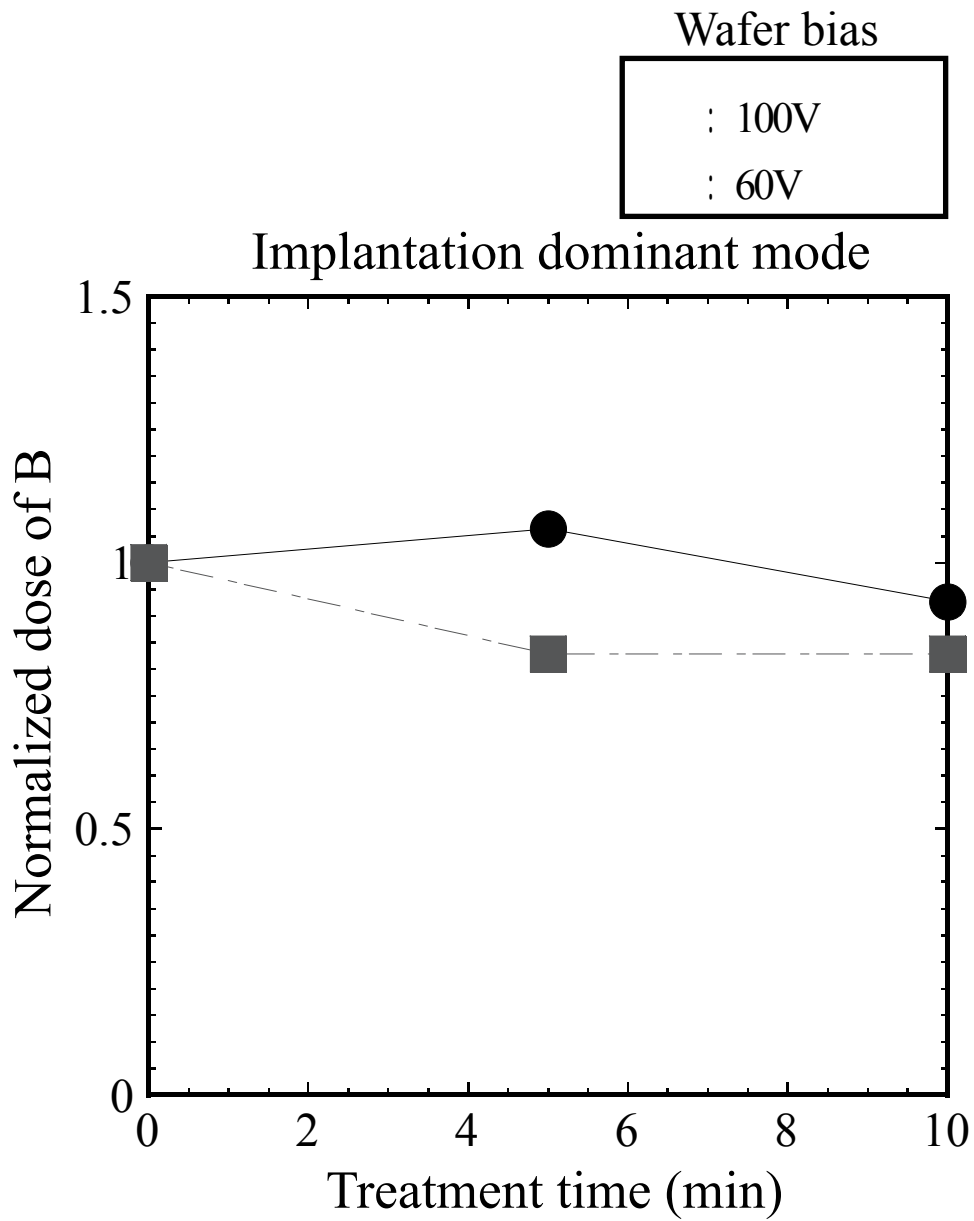
Fig.3.2.11　Dose variation by post APM

treatment . In case of implantation dominant

3.2.7 **APM treatment in the case of "deposition dominant mode"**

Then the dose variation by post APM treatment of "deposition dominant mode" was discussed. The vertical axis was the boron dose normalized by the non-treated references and the horizontal axis was the treatment time.　Zero min. of treatment time meant the non-treated condition and all the data were normalized at this point.　The figure ??? was the results of Dose variation by post APM treatment of the figure ??? was the results of the "deposition dominant mode" .In the case of zero min. of treatment time , sheet resistance was about 73 (ohm / sq) before compensation(wafer bias was 60V).When the wafer bias was 60V, sheet resistance was smaller than bias condition 100V. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 4.5×10^{15} (cm^{-2}). In the 5 min of the APM treatment time the dose was almost the same as large as in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . In the 10 min of the APM treatment time the dose was 60percent smaller than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition . In the 5 min of the APM treatment time the dose was 70 percent larger than in the case of zero min. of treatment time, In bias 60V of Plasma Doping condition . In the 10 min of the APM treatment time the dose was 10 percent larger than in the case of zero min. of treatment time, In bias 60V of Plasma Doping condition. Both case of treatment time in "deposition dominant mode", variation of Boron dose were larger than in the case of "implantation dominant mode".

Fig.3.2.11 variation of sheet resistance by post
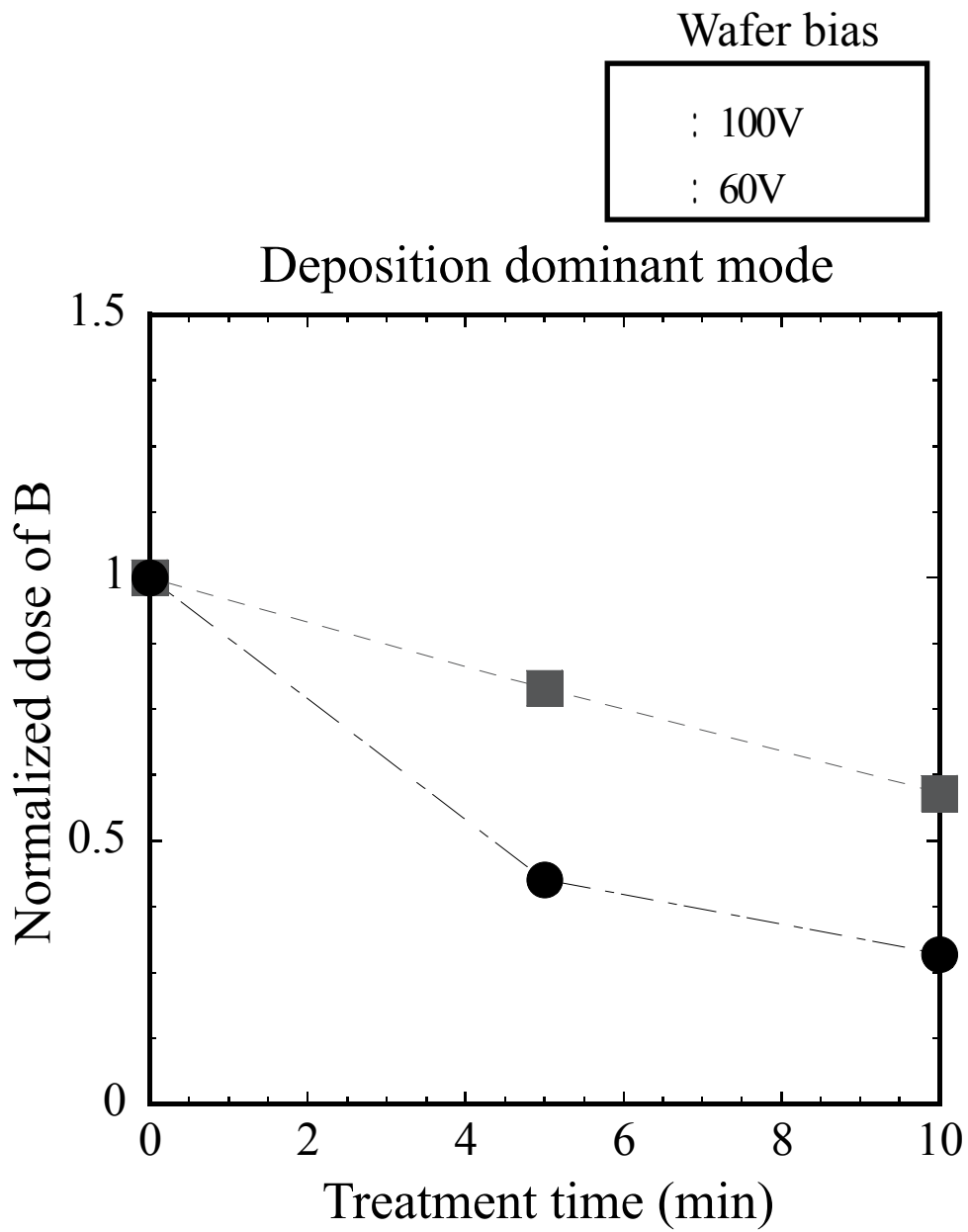
APM treatment . In case of deposition

Fig.3.2.12 Dose variation by post APM

treatment . In case of deposition dominant

3.2.8 Mechanism of the dose increase by the SPM treatment

Mechanism of the dose increase by the SPM treatment is discussed here.   We consider that B atoms are captured in the surface oxide layer and prevented from being lost during the cleaning process as well as the annealing process.   The figure??   shows the supporting evidence to this understanding.   This line shows the increase in dose by the SPM treatment as shown in the previous Figure??.

In the case of zero min. of treatment time , sheet resistance was about 350 (ohm / sq) before compensation in this experiment. When we evaluated dose of Boron from this sheet resistance , Dose of Boron was 3.8×10^{14} (cm^{-2}). In the 5 min of the SPM treatment time the dose was 10 percent larger than in the case of zero min. of treatment time, In bias 100V of Plasma Doping condition .

  The point at the bottom is the sample that had 10min SPM treatment followed by the HF process before annealing. HF treatment time was 5min. The dose decreased drastically in this case. When the sample that had 10min SPM treatment followed by the HF process before annealing , sheet resistance was 560 (ohm / sq). This result indicates that a significant amount of B existed in the surface oxide layer formed by the SPM treatment and they are etched away with the oxide layer by the following HF treatment.
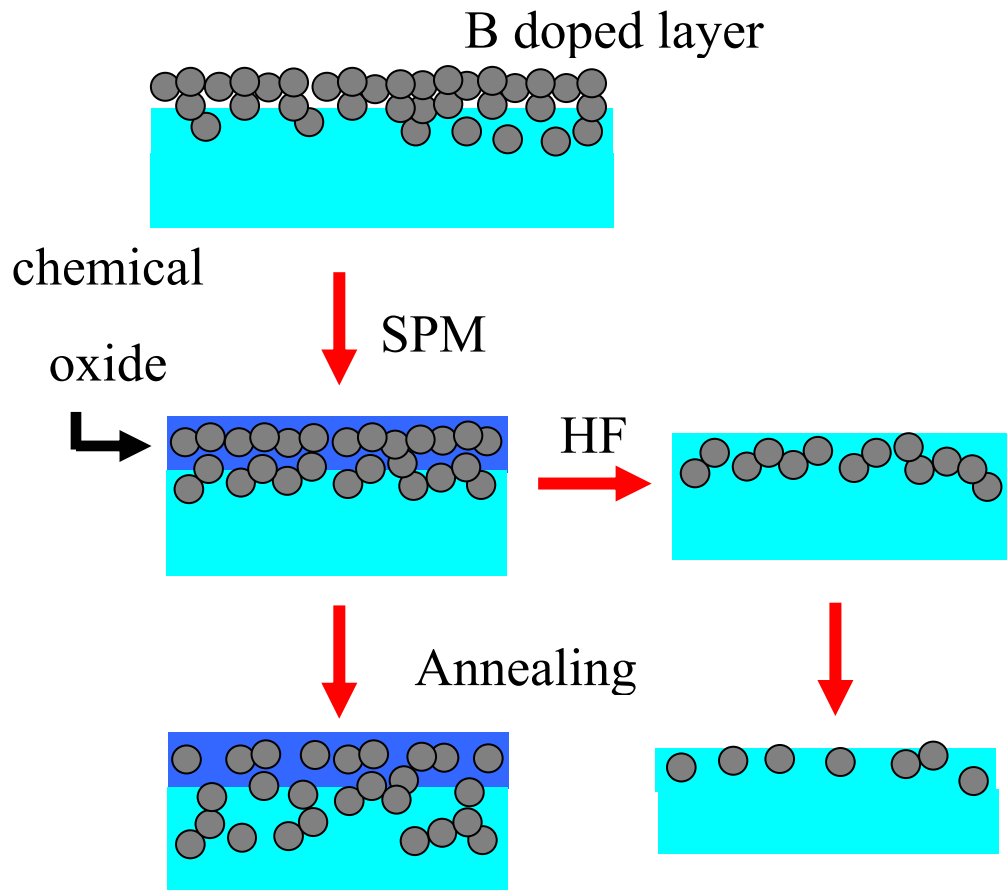
Figure 3.2.13 Prospects of mechanism of the dose

increase by the SPM treatment

B atoms are captured in the surface oxide layer
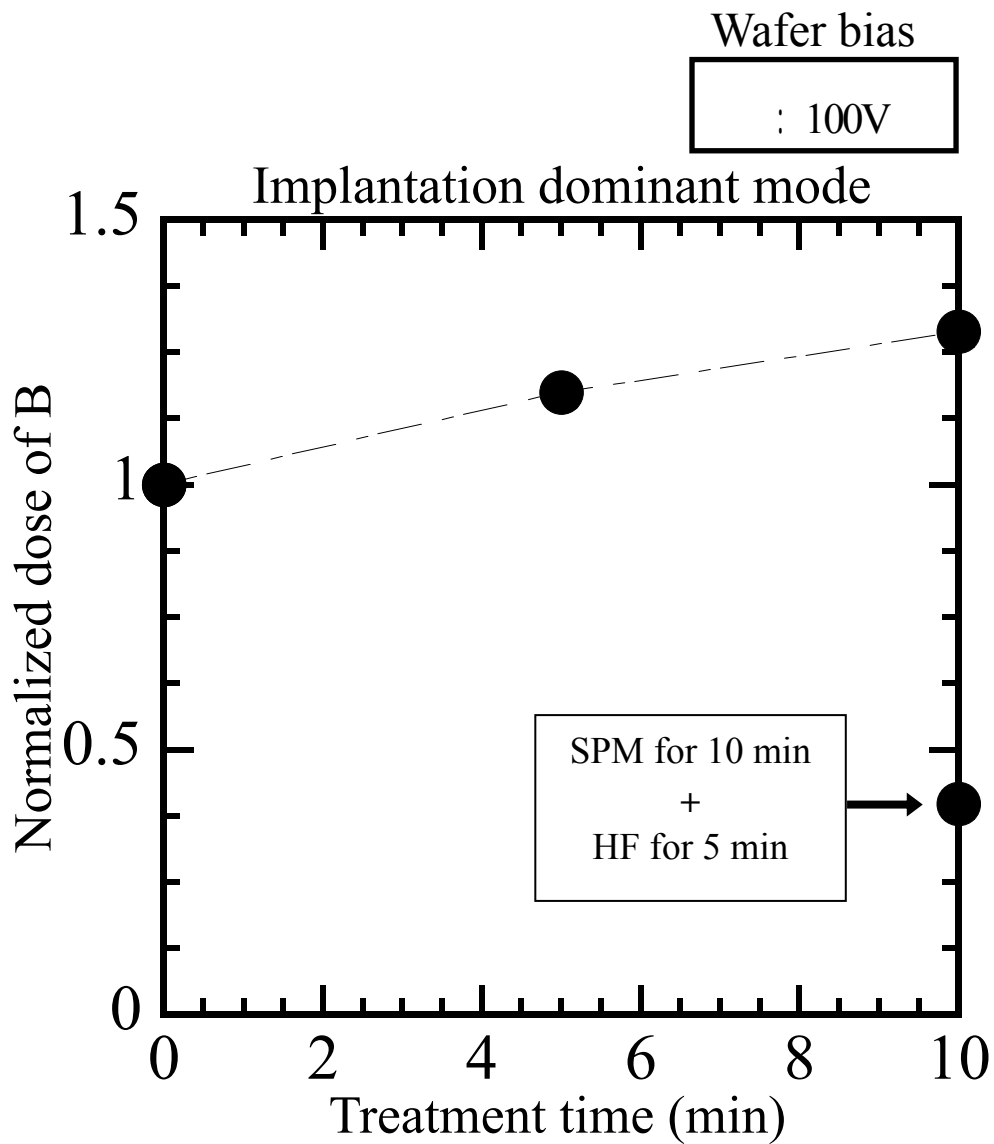
Fig.3.2.14 Mechanism of the dose increase by the SPM treatment

B atoms are captured in the surface oxide layer and prevented from
being lost during the cleaning process and the annealing process.

3.2.9 O₂ thermal treatment

All the while the post cleaning process for plasma doping was affected on dose of impurities; the effect of wet cleaning treatment was investigated in terms of retained dose variation depending on the use of different cleaning chemicals. As the result of wet cleaning treatment on the retained dose of impurities doped by plasma doping, SPM treatment was increased dose significantly. The reason of dose significantly increased by SPM treatment is thought that B atoms are captured in the surface oxide layer and prevented from being lost during the cleaning process and the annealing process. So we tried to another treatment for oxidation except for SPM treatment. In As implantation process Figure ?1 shows sheet resistance depending on O_2 thermal treatment time and Figure ? shows variation of sheet resistance depending on O_2 thermal treatment time.

In totally results of the O_2 thermal treatment after Plasma Doping method, Sheet resistance was smaller than non treatment and better than SPM treatment.

Plasma doping condition was "implantation dominant mode" used in this experiment. Source Power was 1500W. B_2H_6 gas concentration was 0.05%. Wafer bias was 100V. Plasma doping time was 30sec.O2 thermal treatment time were 5min to 20 min. The temperature of O_2 thermal treatment was 500 ^{o}C.

These samples which surface treatment was done were annealed by Rapid Thermal annealing. The reason of such as fast time annealing was to return these data to the latest annealing process like a Flash Lamp Annealing and Spike annealing and Laser annealing method. Long time and very high temperature annealing condition was employed by giving priority to complete electrical activation of boron in order to estimate boron dose from sheet resistance, rather than obtaining shallow junctions. The

sheet resistance were measured by four-point probe method.

In figure ?1 the vertical axis was the variation of sheet resistance and the horizontal axis was the O_2 thermal treatment time.

In the case of samples of zero min. on treatment time sheet resistance was 1017 (ohm / sq) at 900^oC 10second thermal annealing. At 1000^oC 10second thermal treatment, sheet resistance was 355 (ohm / sq) in the case of samples of zero min. on treatment time. At 1100^oC 10second thermal annealing, sheet resistance was 194 (ohm / sq) in the case of samples of zero min. on treatment time. In case of 900^oC 10second thermal annealing, sheet resistance at 5 minutes of O_2 thermal treatment time was 972 (ohm / sq) (this value is untouched.). In the case of 20 minutes. of O_2 thermal treatment time , the result of 20 minutes O_2 thermal treatment time was saturated and as large as 5 minutes.

Figure ? shows variation of sheet resistance depending on O_2 thermal treatment time.

In figure ?2 the vertical axis was the variation of sheet resistance normalized by the non-treated references and the horizontal axis was the O_2 thermal treatment time. Zero min. of treatment time meant the non-treated condition and all the data were normalized at this point.

In the 5 min of the O_2 thermal treatment time, variation of sheet resistance was about 5 percent larger than in the case of zero min. of treatment time. .As the SPM treatment time was 10 minutes and 20 minutes, the variation of sheet resistance was as small as in the case of 5 min. of O_2 thermal treatment time.
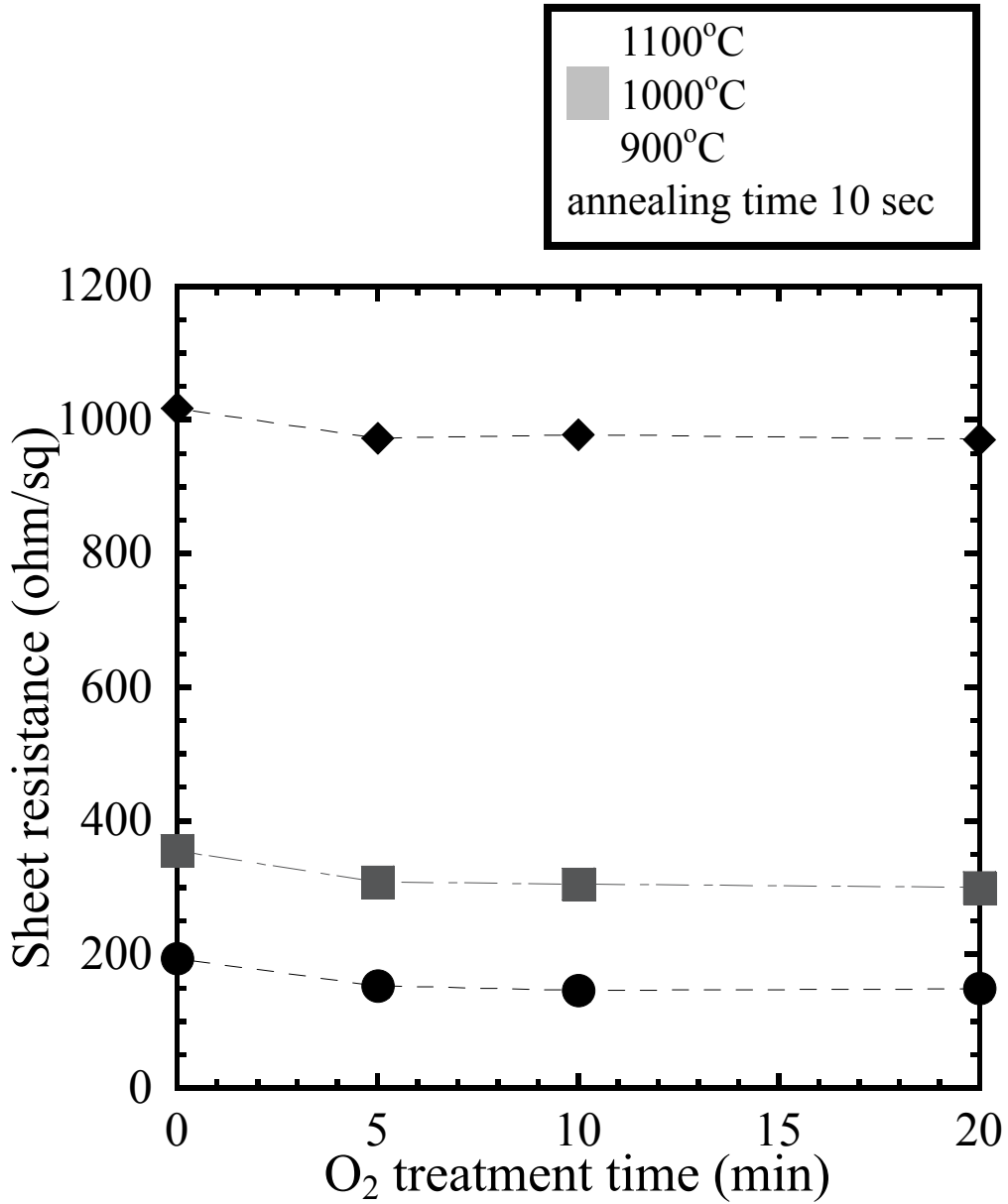
Fig.3.2.15 Variation of sheet resistance

by post O_2 thermal treatment .
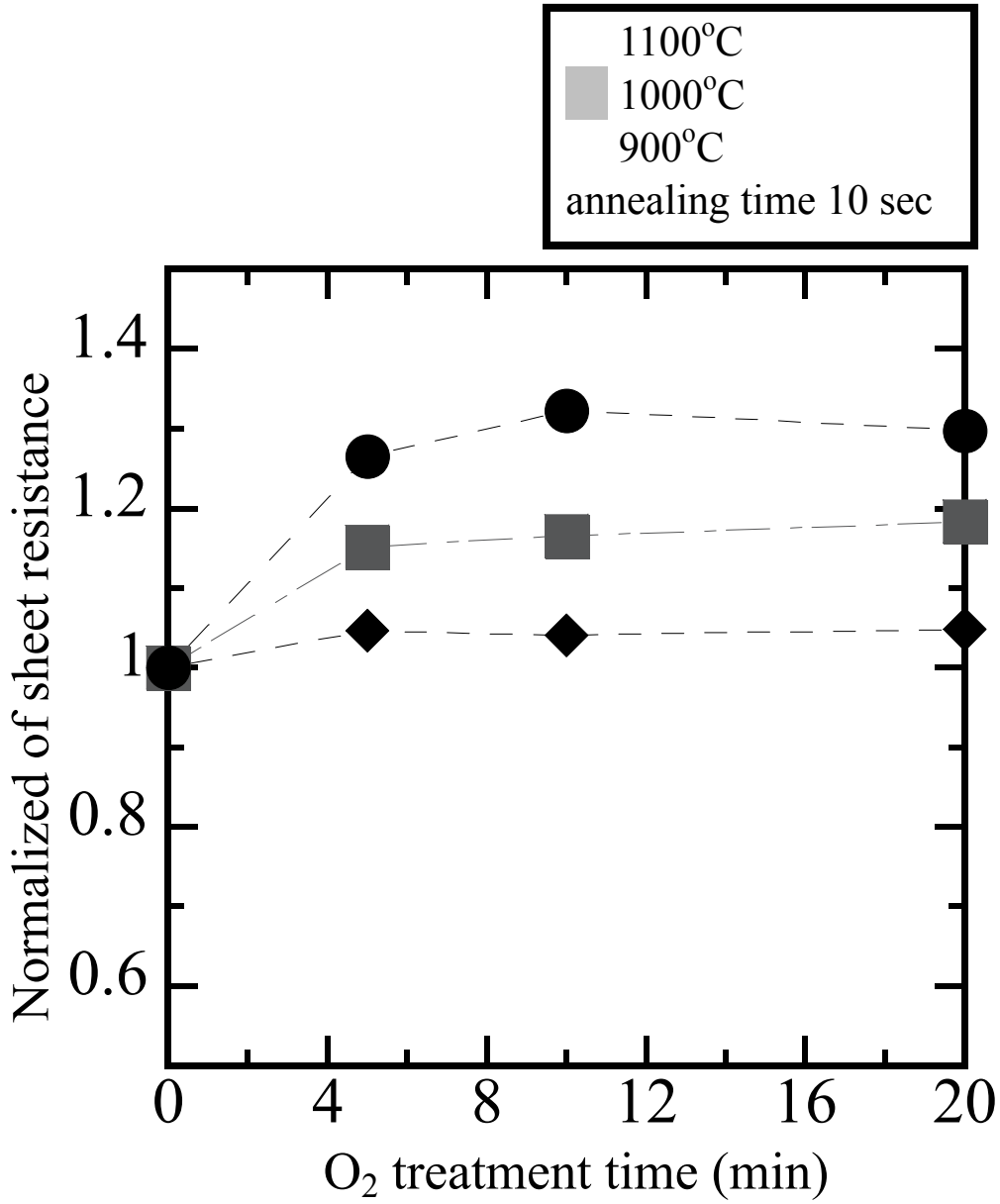
Fig.2.16 Normalized of sheet resistance

by post O_2 thermal treatment .

3.3 Summary of this chapter

HF treatment

B dose largely decreased in this case.

As for the difference between the two doping modes, the decrease in dose was larger on the "deposition dominant mode"

As the HF treatment time was 10 minutes, the dose was about 50 percent larger than in the case of zero min. of treatment time, In several bias of Plasma Doping condition .

APM treatment

In this case, the dose decreased significantly but the change was smaller than that of the HF. Comparing between the two doping modes, it should also be noted that the decrease in dose was larger on the "deposition dominant mode", which is similar to the case of the HF treatment.

SPM treatment

B atoms are captured in the surface oxide layer and prevented from being lost during the cleaning process as well as the annealing process. Significant increase in dose due to the SPM treatment was observed.   Comparing between the two doping modes, the dose increase was larger in the case of the "implantation dominant mode".

O_2 thermal treatment

In totally results of the O_2 thermal treatment after Plasma Doping method, Sheet resistance was smaller than non treatment and similar to SPM treatment.

Chapter 4

Prospect

4.1 Introduction

This chapter is our prospect of our research. Figure shows Mechanism of dose variation by wet cleaning processes of HF, APM, SPM. and thermal treatment.

4.2 Mechanism of dose variation by surface treatment processes

Results of this work were observed as follows. In the case of HF treatment, B dose largely decreased in this case. As for the difference between the two doping modes, the decrease in dose was larger on the "deposition dominant mode"

In the case of APM treatment In this case, the dose decreased significantly but the change was smaller than that of the HF. Comparing between the two doping modes, it should also be noted that the decrease in dose was larger on the "deposition dominant mode", which is similar to the case of the HF treatment.

In the case of B atoms are captured in the surface oxide layer and prevented from being lost during the cleaning process as well as the annealing process. Significant increase in dose due to the SPM treatment was observed.   Comparing between the two doping modes, the dose increase was larger in the case of the "implantation dominant mode".

In the case of O_2 thermal treatment, totally results of the O_2 thermal treatment after Plasma Doping method, Sheet resistance was smaller than non treatment and similar to SPM treatment.

Mechanism of dose variation by wet cleaning processes was considered here. In the case of the SPM treatment, surface oxide layer was formed and a large quantity of boron atoms is captured in the oxide layer as discussed earlier.   The oxide layer prevented the B atoms from escaping during the following annealing process.

On the other hand, in the case of the HF treatment, boron atoms existing in near surface region would be etched away and the deposition layer containing boron atoms would also be washed away.

In the case of the APM treatment, the situation may be somewhere between the SPM and the HF.   The APM treatment is also oxidative, however, the effect of capturing boron may not be so strong and the effect of etching or washing away may be less than that of the HF.
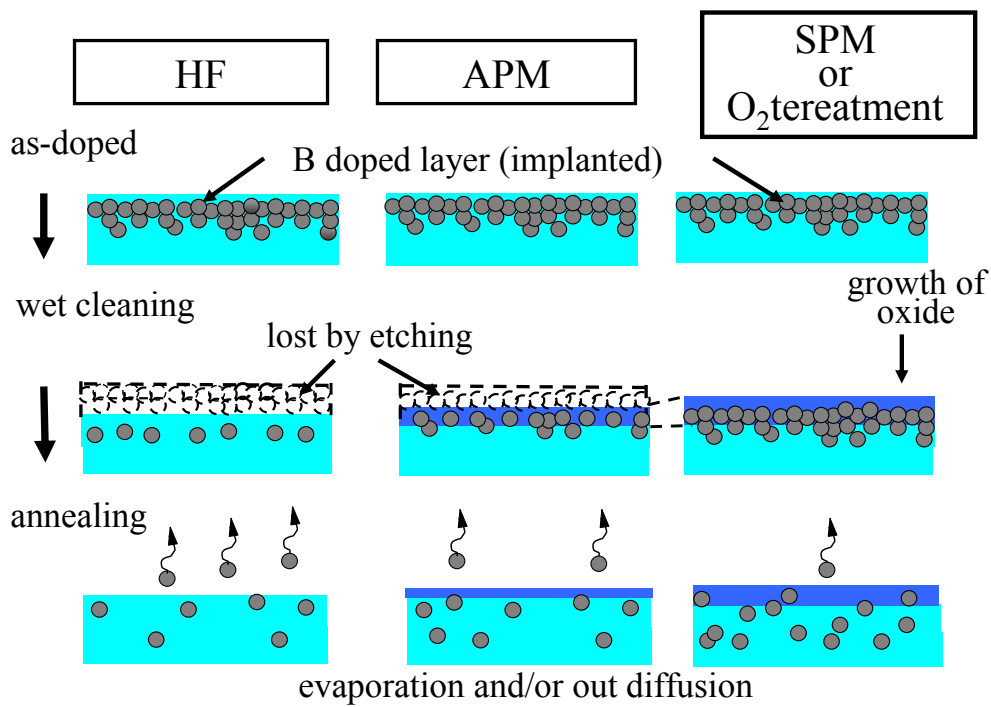
Figure Mechanism of dose variation
by surface treatment processes

4.3 The mechanism of dose variation between the two doping modes

Figure explains the mechanism of dose variation between the two doping modes. The top figure describes the difference in the as-doped profiles.　Let's start with the HF treatment case.　A portion of boron in the surface layer is lost for the implantation dominant mode due to etching of the layer by HF.　On the other hand, for the deposition dominant mode, the majority of deposited B is also lost.　Thus, the relative dose loss would be larger for the deposition dominant mode.

Next, we considered the SPM case.　For the implant dominant mode, the surface oxidation takes place, which effectively captures doped boron atoms.　On the other hand, in the deposition dominant mode, a significant amount of boron in the deposition layer is still lost due to dissolution or etching by the wet process, which reduces the relative increase of boron dose.
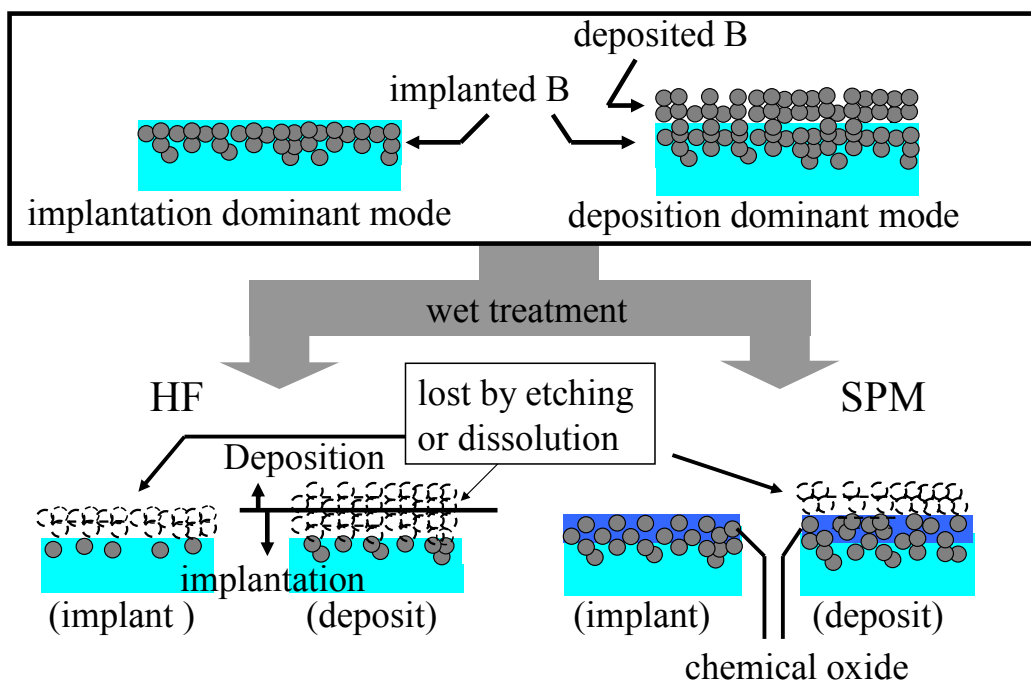
Figure Mechanism of dose variation depending on doping mode

Chapter 5

Conclusion

5.1 Introduction

This chapter is our conclusion. In this chapter, the results obtained from this work are summarized, and conclusions are described.

5.2 Result of our research

Dose variation by post cleaning processes using various wet chemical treatment was studied for Si substrates doped with B by plasma doping.

The effects were significantly different from each other as follows.

SPM / O$_2$ thermal treatment   Dose significantly increased.

HF   Dose largely decreased.

APM   Dose significantly increased.

The oxide layer formed by the SPM treatment captured B atoms and prevented them from being lost during the following annealing process.

The effect of dose decrease is more significant for the "deposition dominant mode". This phenomenon can be attributed to dissolution of the deposited layer by the chemical treatments.

5.3 Forward problem

Plasma doped layer can be susceptible to post cleaning treatment. And Analysis of this doped layer is open problem. So the doped layer is able to be analyzed by XPS or another system to analyze surface layer.

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Appendix

Figure (a) shows Silicon oxide thickness depending on O_2 thermal treatment time. This experiment aimed to how long oxide thickness grew for O_2 thermal treatment. Si wafer which was not done plasma doping was used n-type Silicon and substrate resistance was 8-12 (ohm-cm). Non treatment means that Si wafer was directly used in keeping box. And HF treatment was used to compare with non treatment wafer.

The result is as follows. Silicon oxide thickness was observed by Spectro Ellipsometry. The vertical axis was the Si oxide thickness (nm) and the horizontal axis was O_2 thermal treatment time. Zero minute. of treatment time meant the non-treated condition. In the case of HF last Si oxide thickness at zero minute was 0.2(nm). In the case of non-treatment, Si oxide thickness at zero minute was 1.4(nm).
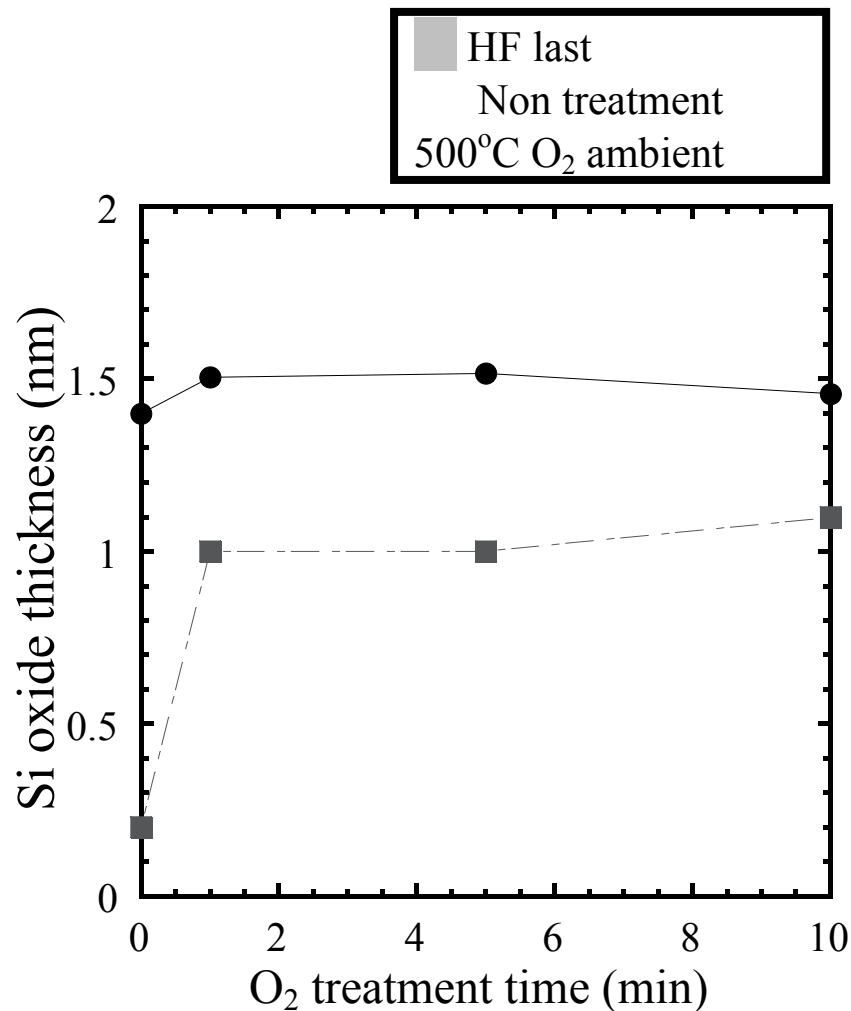

Fig Silicon oxide thickness
depending on O_2 thermal treatment .