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Ultrahigh Vacuum Contactless Capacitance-Voltage
Characterization of Clean and Passivated Silicon Surfaces

Toshiyuki YOSHIDA

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Ultrahigh Vacuum Contactless Capacitance-Voltage Characterization of Clean and Passivated Silicon Surfaces

(超高真空対応非接触容量－電圧法によるシリコンの清浄表面と不活性化表面の評価)

*A Dissertation submitted in partial fulfillment of the requirement for
the degree of Doctor of Philosophy (Engineering) to Hokkaido University*

January, 2001

by

Toshiyuki YOSHIDA

Dissertation Supervisor
Professor Hideki HASEGAWA

Dedicated to
my mother, Sachiko Yoshida,
and my father, Ken-ichi Yoshida

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Chapter 1 Introduction

1.1 Background

1.1.1 History

The information technology (IT) has become an essential and indispensable element in today's information-dominated society. It is expected to become even more important in the society of tomorrow. Electronics based on semiconductor devices such as metal-oxide-semiconductor field effect transistors (MOSFETs) has been one of key technologies to realize this. Further continued progress of this technology is strongly demanded toward the future multi-media society.

For this reason, the history and future trends of MOSFET-based semiconductor technology are briefly reviewed, in the following. Understanding and control of the surface has been one of key issues in the history of semiconductor devices for long time. For example, a concept of a surface field effect transistor based on semiconductors was proposed as early as in 1935. However, as for realization of actual devices, a bipolar transistor using germanium (Ge) was invented first in 1947. Realization of Si-based surface field effect transistor called MOSFETs came much later in 1960's. The reason for this is related to difficulty to form stable insulators on semiconductors with low density of interface states. With Ge, it was practically impossible. On the other hand, the bipolar transistor was not affected so much by the surface conditions. However, once it became possible to form stable SiO_2 film with low interface state densities, the Si-MOSFET became the main unit device of integrated circuits (IC) for the simplicity of the device structure and the low power consumption. This example strongly demonstrates that the surface/interface properties affect device performance drastically, and this is why the study of surface/interface has been one of important subjects for researchers for a long time.

After establishment of suitable technology to control surfaces, the electronics based on silicon devices made great progress very rapidly. This progress of devices is usually represented in terms of the number of devices in integrated circuit (IC). From this viewpoint, ICs have gone through the stages of large scale integration (LSI) and very large scale integration (VLSI), and now we are at present in the stage of the ultra-large scale integration (ULSI). This progress has mostly been brought about by scaling-down of device feature sizes, rough following the scaling-rule proposed by R. H. Dennard *et.al.*¹⁾ in 1974.

As regards the future, the scaling-down is expected or demanded to continue. According to the so-called SIA-road map i.e. International Technology Roadmap for Semiconductors (Semiconductor Industry Association Inc., 1998 Update)²⁾, the integration level and the operation clock frequency of ULSIs at the production level will reach to 64G-bits and 3-4 GHz, respectively early in the 21st century. This requires the gate-length of less than 0.1 μ m and the gate-dielectric thickness of less than 2 nm (in SiO₂). This strongly requires atomic-scale understanding and control of surface/interface properties as a pulling force for further progress of the Si ULSI technology.

For extremely high-frequency operations above several to 10 GHz as required in the optical fiber communication network systems and in the wireless mobile telecommunication network systems, devices based on compound semiconductors such as a high electron mobility transistor (HEMT)³⁾ and a hetero-junction bipolar transistor (HBT)⁴⁾ based on GaAs, InP and their related materials have been successfully developed. Furthermore, novel quantum effect devices such as quantum wire transistors and single electron transistors⁵⁾ have been successfully demonstrated their extremely low delay-powered products using compound semiconductors.

However, Si-based electronic devices are also making progress towards high speed and low power, and similar to those of compound semiconductor devices have been demonstrated at research levels. For example, the cut-off frequency of a MOSFET can be reached to a few hundred GHz^{6,7)} by using an ultrathin oxide film (<1.5 nm) formed by rapid thermal processing; photo- or electro-luminescence with

visible wave-length could be observed using the porous Si^{8,9}); there are some predictions to realize hetero-structures by introducing SiGe^{10,11}) or SiC; Si-based single electron transistors were realized using silicon on insulator (SOI)¹²), and so on. Thus, the Si-based electronic devices will perform not only the role of the key devices in the future ULSI technology, but will compete with compound semiconductor technologies in high-speed nanoelectronics area. Here, again continued study for Si surfaces is strongly required.

1. 1. 2 Monitoring of silicon surface properties

To further advance the Si complementary metal-oxide-semiconductor (CMOS) technology to its ultimate scaling limits as well as to develop new nano-devices such as Si-based single electron transistors, it becomes increasingly important to understand and to control delicate changes of Si surface properties due to nano-structure processing. Since all processing steps for semiconductor device fabrication are usually carried out on or through surfaces, electronically active near-surface defects introduced during processing can deteriorate the performance of nano-devices which are extremely sensitive to surfaces and interfaces. According to SIA-road map, it needs to characterize and control the surface defects in the order of 10^{10} cm^{-2} in near future.

Hydrogen terminated Si surface is generally used as an initial surface for ultrathin insulator formation process because of its flatness and cleanness in atomic-scale. And this surface can be obtained easily by dipping into HF/NH₄F-related solutions. In recent years, surface science type techniques such as x-ray photoelectron spectroscopy (XPS)¹³), scanning tunneling microscopy (STM)/atomic-force microscopy (AFM)^{14,15}), Fourier transform infrared-absorption spectroscopy (FTIR)^{16,17}), grazing angle x-ray diffraction (XRD)¹⁸), etc. have made great progress in characterization of chemical compositions and microscopic structures of hydrogen terminated and ultrathin insulator covered surfaces. So far, capacitance-voltage (C-V) method had been used to characterize the electronic properties of interface, but this

method fails due to Schottky or tunneling MIS conduction in today's ultrathin region of thickness. Instead of this, total-photoelectron-yield spectroscopy^{19,20}, scanning capacitance microscopy (SCaM)²¹⁻²⁴, etc. were applied to characterize the electronic properties of free and ultrathin insulator covered surfaces. However, *in-situ* and quantitative characterization of electronic properties has not been made yet.

Here, some examples are described below about necessity of characterization of electronic properties. For hydrogen terminated Si surface, the calculation results using first-principle molecular dynamics show that no surface states is appeared in forbidden gap when all of surface Si dangling-bonds are terminated by hydrogen atoms. This result indicates that an ideal passivated Si surface can be obtained using hydrogen termination process. However, there was no established method to characterize the surface state density distribution of hydrogen terminated Si surface, which has prevented us from further optimization of hydrogen termination process. In case of ultrathin insulator/Si interface, there are some predictions about the relationship between the electronic interface properties and the amount of suboxide components or the existence of nitrogen atoms at the interface. Many experimental results were reported about chemical compositions, stoichiometric analyses, surface roughness, etc. However, the interface state density distributions have not been determined yet directly and quantitatively.

Thus, it is now strongly required to develop new technique to characterize the electronic properties of free and ultrathin insulator covered Si surfaces in non-destructive fashion. And the optimization of processing conditions is necessary by synthetic analyses of electronic, chemical, optical and structural properties.

1.2 Objective of present work

For realization of excellent properties of ultrathin insulator/Si interface, it becomes increasingly important to optimize the processing conditions including initial surface condition with monitoring all of electronic, chemical, optical and structural properties. Hydrogen terminated silicon surface is most suitable, in this stage, for initial

surface. In 1993, the contactless *C-V* technique was developed by Sakai *et al.*²⁵⁾ (Dainippon Screen Mfg. Co., Ltd.) for the characterization of electronic properties of semiconductor surfaces. Using this technique, the contactless and non-destructive characterization of electronic properties such as doping density, surface/interface state density etc can be carried out in atmospheric environment. Furthermore, this contactless *C-V* technique was extended to UHV contactless *C-V* system by our research group²⁶⁾, and the *in-situ* monitoring of surface electronic properties before and after various kinds of UHV-based processing steps become possible, for the first time.

The purpose of this thesis is to characterize and to optimize the formation processes of initial surfaces and ultrathin passivation layers with the use of UHV contactless *C-V*, XPS, photoluminescence surface state spectroscopy (PLS³) and AFM measurements. The concrete purposes are as follows.

- (1) To describe capabilities of a novel UHV contactless *C-V* method which our research group has recently developed.
- (2) Characterization and optimization of the electronic properties of hydrogen terminated silicon surfaces formed by HF/NH₄F-based chemical solutions.
- (3) Investigation of thermal stability of optimized hydrogen terminated Si surface in UHV environment.
- (4) Characterization and optimization of properties of ultrathin insulator/Si interface with the use of UHV contactless *C-V*, XPS and PLS³ techniques.

1.3 Synopsis of each chapter

This thesis consists of six chapters.

Chapter 1 is the introduction of this work.

In *Chapter 2*, a conventional standard MIS C - V theory²⁷⁾ is described for ideal case prior to the explanation of the UHV contactless C - V technique. The story is extended to the practical MIS structure with oxide fixed charges and interface trapped charges. Particularly, the existence of interface traps deteriorate the almost all the semiconductor device performances because of "Fermi level pinning." The interface trap is also called as the interface state. Characterization and reduction of interface state density are now one of key issues for further prosperity of present semiconductor technology. To do this, the combine use of characterizations of electronic, chemical, optical and structural properties is important. Contactless C - V , XPS, PLS³ and AFM are used, in this study, for electronic, chemical, optical and structural characterization, respectively. In this chapter, the principles of characterization method of interface state density based on C - V measurement²⁸⁾ is described together with the explanations of XPS, PLS³ ²⁹⁻³¹⁾ and AFM methods.

In *Chapter 3*, a novel UHV contactless C - V method²⁶⁾ is described. In recent years, the thickness of insulator layer for gate dielectric has been reduced to a few nano-meter region. Especially in G-bit DRAM, the thickness of SiO_2 layer become less than 3 nm. In this region, direct tunneling current can not be ignored, which leads the conventional MIS C - V theory in failure. This can be avoided by introducing an "UHV-gap" between the field electrode and the sample surface, i.e. the field electrode is separated from the sample surface. By using this system, the C - V measurement can be applied to ultrathin insulator covered surfaces as well as to bare semiconductor surfaces without any insulator layer. The UHV-gap length is one of important parameters for the accurate analysis of obtained C - V curve. In this system, the UHV-gap length can be accurately determined by measuring the variation of reflectance of laser light due to Goos-Hächen effect³²⁾. Furthermore, this system is connected to UHV-based multi-chamber-system equipped in the super-clean room of the Research Center for Interface Quantum Electronics (RCIQE), Hokkaido University. This

method seems to be very powerful for *in-situ* electronic characterization of "free" and/or "processed" semiconductor surfaces.

In **Chapter 4**, various kinds of hydrogen terminated silicon surfaces are characterized by combine use of UHV contactless *C-V*, XPS, PLS³ and AFM measurements. For the hydrogen termination, Si wafers were treated in HF- or NH₄F-based solutions. After hydrogen termination, no-oxide component was detected by XPS measurement, and terrace-step structures were clearly appeared on NH₄F treated (111) surface. These results indicates that the atomically flat and clean surfaces can be obtained after hydrogen termination. However, from UHV contactless *C-V* analyses, hydrogen terminated surface possesses a fast discrete surface state at around 0.6-0.7 eV from valence band edge (E_V) and slow states which cause a large hysteresis in *C-V* curve. By the sufficiently long NH₄F treatment, the discrete states disappeared, and the hysteresis in *C-V* curve drastically reduced after annealing in UHV at 200 °C. Thus, a UHV-compatible completely passivated surface could be obtained. The most likely origin of fast surface states is Si-dangling bond not terminated by hydrogen, and that of slow surface states is excess hydrogen.

In **Chapter 5**, various kinds of ultrathin oxide or oxynitride/Si interfaces were characterized by UHV contactless *C-V*, XPS and PLS³ measurements. To form ultrathin oxide layer, oxidation by chemical solution such as HNO₃, H₂SO₄:H₂O₂, and low-temperature (400°C) thermal oxidation were carried out, and these processes gave oxide layers with thickness of about 1 nm. Limited capacitance variations and low photoluminescence (PL) efficiencies were observed in all of ultrathin oxide/Si interfaces studied in this work, indicating the existence of high interface state density and strong Fermi level pinning. Additional N₂ plasma treatment had no effect on the interface properties. On the other hand, marked enhancement of *C-V* variation and PL efficiency was achieved at the surface after ECR-N₂O plasma oxynitridation at 400 °C. Formation of a phase separated Si/Si₃N₄/SiO₂ structure and the reduction of suboxide components seem to improve the interface properties.

In (100)-oriented surface, there is no well-established hydrogen termination technique in spite of its usefulness for today's manufacturing. In this work, H₂ plasma cleaning process was tried to realize oxide-free well-defined hydrogen terminated (100) surface. For the (100) surface after H₂ plasma cleaning process, no oxide component was detected by high-resolution XPS analyses. There were only Si-H and Si-H₂ component. On the other hand, the surface without H₂ plasma cleaning process possesses oxide component clearly. This difference affects to following ECR-N₂O plasma oxynitridation. The oxynitridation process with H₂ plasma cleaning process formed relatively well-behaved ultrathin oxynitride/Si interface with the minimum value of interface state density of $1 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$, while that without H₂ plasma cleaning process gave the minimum value of density of $4\text{-}6 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$. The ECR-N₂O plasma process produces, at first stage, nitride component (similar to Si₃N₄). The residual oxide component existing at the initial surface was taken into this nitride-formation process, leading formation of oxynitride phase. This oxynitride phase disturbs the phase separation of Si/Si₃N₄/SiO₂, affecting the interface properties.

Chapter 6 summarizes the present work and gives the conclusion.

References

- 1) R. H. Dennard, F. H. Gaensslen, H. N. Yu, V. L. Rideout, E. Bassous and A. R. Leblanc: IEEE Solid-State Circuits **SC-9** (1974) 256.
- 2) International Technology Roadmap for Semiconductors, 1998 Update, by the Semiconductor Industry Association Inc.
- 3) T. Mimura, S. Hiyaizumi, T. Fujii and K. Nambu: Jpn. J. Appl. Phys. **19** (1980) L225.
- 4) E. J. Caine, S. Subbanna, H. Kroemer, J. L. Merz and A. Y. Cho: Appl. Phys. Lett. **45** (1984) 1123.
- 5) K. K. Likhsrev: IBM J. Res. Develop. **32** (1988) 144.
- 6) H. S. Momose, M. Ono, T. Ohguro, S. Nakamura, M. Saito and H. Iwai: IEDM Tech. Dig. (1994) 593.
- 7) H. Iwai and H.S. Momose: IEDM Tech.Dig. (1998) 163.
- 8) H. Mizuno, H. Koyama and N. Koshida: Appl. Phys. Lett. **69** (1996) 3779.
- 9) H. Mizuno and N. Koshida: Mater. Res. Soc. Symp. Proc. **536** (1999) 179.
- 10) S. S. Iyer *et al.*: IEDM Tech. Dig. (1987) 874.
- 11) G. L. Patton *et al.*: Symp. VLSI Tech. (1989) 95.
- 12) K. Shiraishi *et al.*: Physica E **7** (2000) 337.
- 13) K. Ohnishi and T. Hattori: Jpn. J. Appl. Phys. **33** (1994) L675.
- 14) R. S. Becker, G. S. Higashi, Y. J. Chabal and A. J. Becker: Phys. Rev. Lett. **65** (1990) 1917.
- 15) Y. Morita, K. Miki and H. Tokumoto: Appl. Phys. Lett. **59** (1991) 2187.
- 16) G. S. Higashi, Y. J. Chabal, G. W. Trucks and K. Raghavachari: Appl. Phys. Lett. **56** (1990) 656.
- 17) T. Takahagi, I. Nagai, A. Ishitani, H. Kuroda and Y. Nagasawa: J. Appl. Phys. **64** (1988) 3516.
- 18) A. Ourmazd and P. H. Fuoss: Appl. Surf. Sci. **41/42** (1989) 365.
- 19) K. Winer, I. Hirabayashi and L. Ley: Phys. Rev. B **38** (1988) 7680.
- 20) S. Jin and L. Ley: Phys. Rev. B **44** (1991) 1066.
- 21) C. C. Williams, W. P. Hough and S. A. Rishton: Appl. Phys. Lett. **55** (1989) 203.

- 22) C. C. Williams, J. Slinkman, W. P. Hough and H. K. Wickramasinghe: Appl. Phys. Lett. **55** (1989) 1662.
- 23) H. Tomiye, H. Kawami, M. Izawa, M. Yoshimura and T. Yao: Jpn. J. Appl. Phys. **34** (1995) 3376.
- 24) H. Tomiye, T. Yao, H. Kawami and T. Hayashi: Appl. Phys. Lett. **69** (1996) 4050.
- 25) T. Sakai, M. Kohno, S. Hirae, I. Nakatani and T. Kusuda: Jpn. J. Appl. Phys. **32** (1993) 4005.
- 26) T. Yoshida, H. Hasegawa and T. Sakai: Jpn. J. Appl. Phys. **38** (1999) 2349.
- 27) S. M. Sze: Physics of Semiconductor Devices, (John Wiley & Sons, New York, 1981), 2nd Ed.
- 28) E. H. Nicollian and J. R. Brews: MOS(Metal Oxide Semiconductor) Physics and Technology (Wiley, New York, 1982) 319.
- 29) T. Saitoh, H. Iwadate and H. Hasegawa: Jpn. J. Appl. Phys. **30** (1991) 3750.
- 30) T. Saitoh and H. Hasegawa: Appl. Surf. Sci. **56-58** (1992) 94.
- 31) T. Sawada, K. Numata, S. Tohdoh, T. Saitoh and H. Hasegawa: Jpn. J. Appl. Phys. **32** (1993) 511.
- 32) F. Goos and H. Hanchen: Ann. Phys. **6** (1947) 344.

Chapter 2 Physics and Characterization Methods of Insulator-Semiconductor Interfaces

2.1 Introduction

The study of the physics of semiconductor surfaces and insulator-semiconductor (I-S) interfaces is one of key issues for a sheer scientific interest as well as for further improvement of semiconductor-based electronic devices such as silicon metal-insulator-semiconductor (MIS) field-effect-transistors (FETs) and recent semiconductor-based quantum effect devices.

The electronic properties such as conduction type, doping density, density of oxide-fixed charge, surface/interface state density distribution and surface/interface Fermi level position are the important characteristics for the today's semiconductor-based devices. Especially, the existence of large amount of surface/interface states causes "Fermi level pinning" which directly affects to device performances. The basic principle of the semiconductor-based electronic devices such as MISFETs is to control the surface condition changing the surface Fermi level position. The "Fermi level pinning" phenomenon prevents this. Thus, it is very important to characterize the surface/interface state density distribution together with other properties such as chemical and optical properties and surface atomic-scale structure.

The ultrahigh vacuum (UHV) contactless capacitance-voltage ($C-V$)^{1,2}, x-ray photoelectron spectroscopy (XPS), photoluminescence surface state spectroscopy (PLS)³⁻⁵ and atomic force microscopy (AFM) measurements have been carried out, in this study, to characterize the electronic/chemical/optical properties as well as to observe the surface atomic-scale structure. In this chapter, the detail principle, theory and practice measurement system of these characterization methods are described.

Here, prior to understand the principle of UHV contactless C - V method, it needs to understand the basic MIS C - V theory^{6,7}). The detail explanations of the UHV contactless C - V method are described in chapter 3.

Additionally, the model of surface/interface state and the pinning mechanism of Fermi level are also described based on disorder-induced-gap-state (DIGS) model⁸).

2.2 Definition of ideal metal-insulator-semiconductor (MIS) structure

The ideal metal-insulator-semiconductor (MIS) structure can be defined as follows.

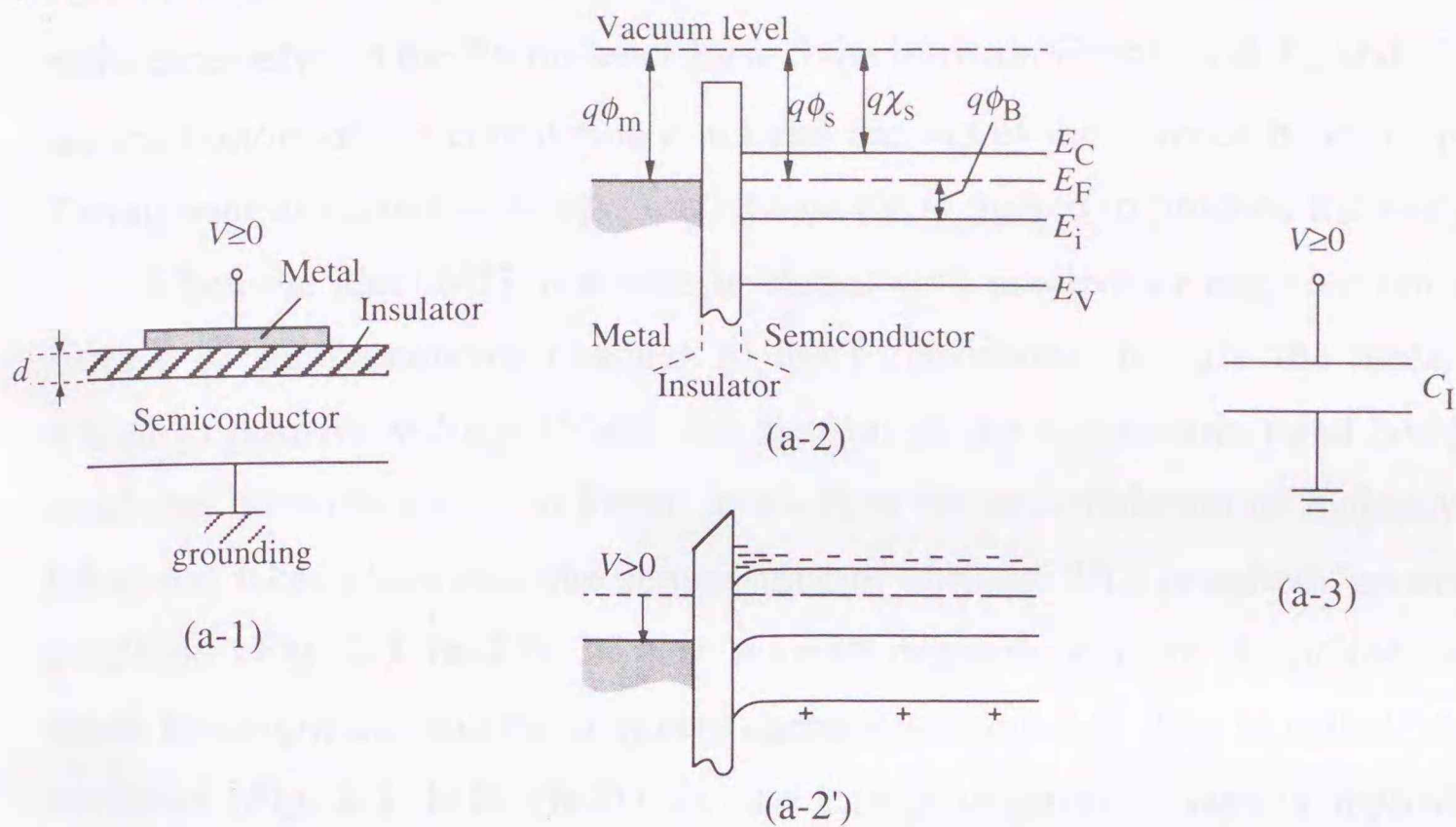
- (1) At zero applied bias, energy difference between the metal work-function and the semiconductor work-function is zero, or the band is flat when there is no applied voltage.
- (2) The only charges that can exist in the structure under any biasing conditions are those in the semiconductor and those with the equal but opposite sign on the metal surface adjacent to the insulator.
- (3) There is no carrier transport through the insulator under dc biasing conditions, or the resistivity of the insulator is infinity.

In the whole of this dissertation, *ideal* structure, *ideal* condition, ... signify meeting above three requirements.

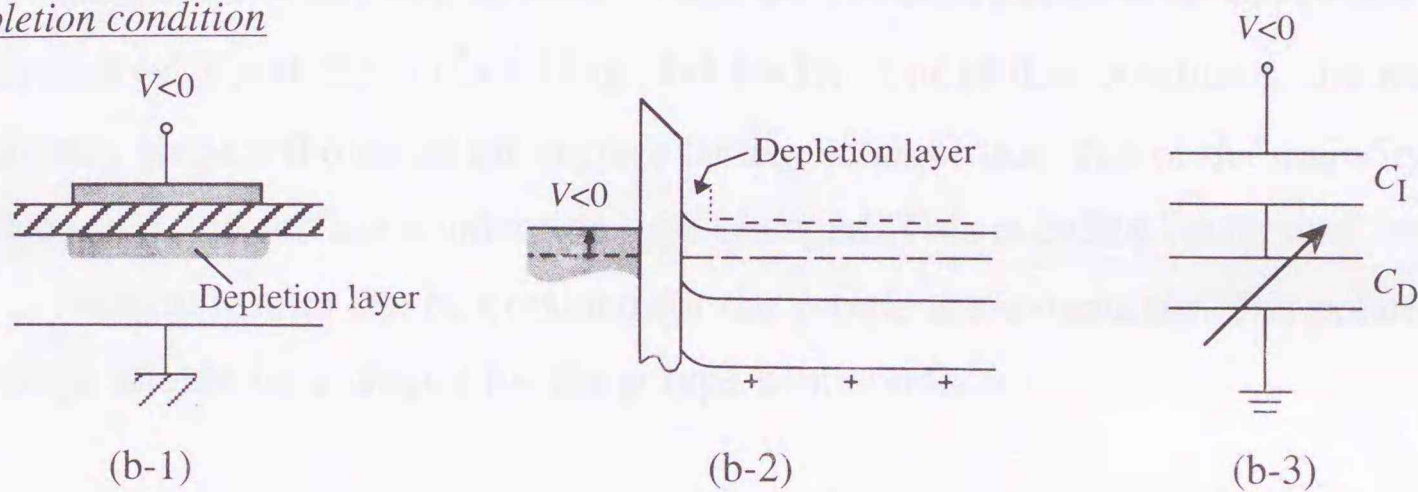
2.2.1 Energy band diagram and surface charge

The MIS structure is shown in **Fig. 2-1 (a-1)**, where d is the thickness of the insulator layer and V is the applied voltage on the metal field plate. When V is positive (negative) value, the metal plate is positively (negatively) biased with respect to the grounding. The energy-band diagram of MIS structure at $V=0$ is shown in **Fig. 2-1 (a-2)** (flat-band condition), where ϕ_m is the metal work-function, χ is the semiconductor electron affinity, ϕ_s is the semiconductor work-function, ϕ_B is the potential

Flat-band and accumulation conditions



Depletion condition



Inversion condition

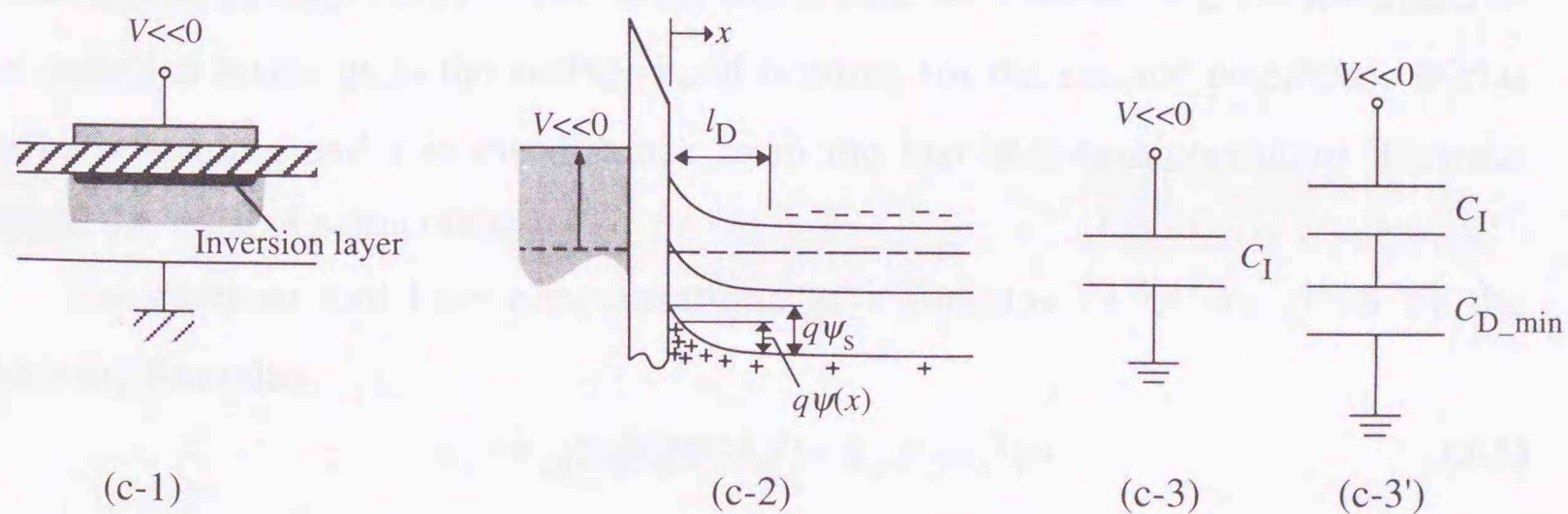


Fig. 2-1 Schematic view of ideal MIS structure, energy-band diagram and equivalent circuit under zero or positive bias voltage (a-1,2,3), weak negative bias voltage (b-1,2,3) and strong negative bias voltage (c-1,2,3).

difference between the Fermi level E_F and the intrinsic Fermi level E_i , and E_C and E_V are the bottom of the conduction band and the top of the valence band, respectively. Throughout this chapter, n-type semiconductor is treated to proceed the story.

When the ideal MIS structure is biased with positive or negative voltages, the surface of semiconductor changes to three conditions. In case the metal plate is biased to positive voltage ($V > 0$), the bottom of the conduction band bends downward and becomes closer to Fermi level, then the accumulation of majority carriers (electron) takes place near the semiconductor surface. This is called "accumulation" condition (**Fig. 2-1 (a-2')**). In case a small negative voltage is applied ($V < 0$), the bands bend upward, and the majority carriers are depleted. This is called "depletion" condition (**Fig. 2-1 (b-1), (b-2)**). In case a large negative voltage is applied, finally, the bands bend even more upward so that the intrinsic Fermi level E_i crosses over the Fermi level E_F at the surface (**Fig. 2-1 (c-2)**). Under this condition, the number of minority carriers (holes) at the surface becomes larger than that of the majority carriers (electrons), the surface conduction type changed. This is called "inversion" condition.

Similar results can be obtained for the p-type semiconductor. The polarity of the voltage should be changed for the p-type semiconductor.

Here, the quantitative analysis for the surface carrier density is discussed. In **Fig. 2-1 (c-2)**, the symbols used in following discussion are shown, l_D is the thickness of the depletion layer, ψ_s is the surface band bending (or the surface potential), $\psi(x)$ is the band bending and x is the distance from the insulator-semiconductor interface toward the bulk of semiconductor.

The electron and hole concentrations as a function of ψ are given by the following formulae

$$n_n = n_{n0} \exp(q\psi / kT) = n_{n0} \exp(\beta\psi) \quad (2-1)$$

$$p_n = p_{n0} \exp(-q\psi / kT) = p_{n0} \exp(-\beta\psi) \quad (2-2)$$

where n_{n0} and p_{n0} are the equilibrium densities of electrons and holes, respectively, in the bulk of the semiconductor, k is Boltzmann's constant, T is the absolute temperature, and $\beta \equiv q / kT$. At the surface, these densities are written by

$$n_s = n_{n0} \exp(\beta \psi_s) \quad (2-3)$$

$$p_s = p_{n0} \exp(-\beta \psi_s). \quad (2-4)$$

Surface conditions described previously can be rewrote as follows

$\psi_s > 0$	accumulation condition (bands bend downward)
$\psi_s = 0$	flat-band condition
$\psi_B < \psi_s < 0$	depletion condition (bands bend upward)
$\psi_s = \psi_B$	midgap with $n_s = p_s = n_i$ (n_i is intrinsic concentration)
$2\psi_B < \psi_s < \psi_B$	inversion condition (weak inversion: minority carrier appear at the surface)
$\psi_s \leq 2\psi_B$	inversion condition (strong inversion: a number of minority carrier becomes same as or larger than that of majority carrier of the bulk).

The relationship between surface carrier density and the surface potential distribution under dc bias condition is written as following, utilizing the one-dimensional Poisson's equation,

$$\frac{d^2 \psi(x)}{dx^2} = -\frac{\rho(x)}{\epsilon_s \epsilon_0} \quad (2-5)$$

where ϵ_0 is permittivity of vacuum, ϵ_s is permittivity of semiconductor and $\rho(x)$ is the total space-charge density given by

$$\rho(x) = q(N_d - N_a + p - n) \quad (2-6)$$

where q is the elementary charge, N_d and N_a are the donor and the acceptor density, respectively, and p and n are the hole and electron densities, respectively. In the bulk of the semiconductor, charge neutrality must exist, or $\rho(x)=0$ and $\psi=0$, then we have

$$N_d - N_a = n_{n0} - p_{n0}. \quad (2-7)$$

Furthermore, from Eqs. (2-1) and (2-2), we have

$$p_n - n_n = p_{n0} \exp(-\beta \psi) - n_{n0} \exp(\beta \psi). \quad (2-8)$$

Finally, the Poisson's equation to be solved is

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{q}{\epsilon_0 \epsilon_s} [p_{n0} \{\exp(-\beta\psi) - 1\} - n_{n0} \{\exp(\beta\psi) - 1\}]. \quad (2-9)$$

Integrating Eq. (2-9) from the bulk toward the surface gives the electric field, E , as follows

$$E = -\frac{\partial \psi}{\partial x} = \pm \frac{\sqrt{2}}{\beta L_D} \cdot F\left(\beta\psi, \frac{p_{n0}}{n_{n0}}\right) \quad (2-10)$$

where

$$L_D = \sqrt{\frac{kT\epsilon_0\epsilon_s}{n_{n0}q^2}} \quad (2-11)$$

$$F\left(\beta\psi, \frac{p_{n0}}{n_{n0}}\right) = \left[\frac{p_{n0}}{n_{n0}} \{\exp(-\beta\psi) - \beta\psi - 1\} - \{\exp(\beta\psi) + \beta\psi - 1\} \right]^{1/2} \quad (2-12)$$

here, L_D is called the extrinsic Debye length for electrons. Then, by using the Gauss's law, the space charge density to produce this electric field is given by

$$Q_s = -\epsilon_0 \epsilon_s E_s = \mp \frac{\sqrt{2} \epsilon_0 \epsilon_s kT}{q L_D} \cdot F\left(\beta\psi_s, \frac{p_{n0}}{n_{n0}}\right). \quad (2-13)$$

The relationship between the surface potential and the space-charge density in the semiconductor obtained from Eq. (2-13) is plotted in **Fig. 2-2**. An n-type silicon is chosen as an example with various carrier concentrations at room temperature. We can see the difference between the weak inversion condition and the strong inversion condition from the slope of curves.

2. 2. 2 Differential capacitance and ideal capacitance-voltage (C-V) characteristics

As shown in previous discussion, the MIS structure can store charge by applying the positive or negative bias on the metal plate, thus, it forms so-called "MIS capacitor". Because charge on an MIS capacitor varies with voltage nonlinearly, the capacitance value of this MIS capacitor can not be defined by the conventional

static capacitance. The *differential* capacitance must be defined as

$$C_{\text{diff}} \equiv \frac{dQ}{dV}. \quad (2-14)$$

From measuring the differential capacitance, the rate of change of charge with voltage at the semiconductor surface can be determined, which gives us important informations in the view point of device driving (described later).

The total capacitance of MIS capacitor is given by series connection of the insulator capacitance, C_I , and the capacitance of depletion layer of semiconductor, C_D ,

$$\frac{1}{C} = \frac{1}{C_I} + \frac{1}{C_D(\psi_s)}. \quad (2-15)$$

The insulator capacitance, C_I , can be determined as a static capacitance, $C_I = \epsilon_0 \epsilon_1 / d$, and the depletion layer capacitance, C_D , must be determined as a differential capacitance, so Eq. (2-14) can be rewrote as

$$C_D(\psi_s) \equiv \frac{dQ_s}{d\psi_s}. \quad (2-16)$$

From Eqs. (2-13) and (2-16),

$$C_D(\psi_s) = \frac{\epsilon_0 \epsilon_s}{\sqrt{2} L_D} \frac{1 - \exp(-\beta\psi_s) + \frac{p_{n0}}{n_{n0}} \{\exp(\beta\psi_s) - 1\}}{F\left(\beta\psi_s, \frac{p_{n0}}{n_{n0}}\right)} \quad (2-17)$$

At flat-band condition, $\psi_s=0$, both of the denominator and the numerator of Eq. (2-17) become to zero. So C_D can be obtained by expanding the exponential terms into series, then

$$C_D|_{\psi_s=0} = \frac{\epsilon_0 \epsilon_s}{L_D} \sqrt{1 + \frac{p_{n0}}{n_{n0}}} \approx \frac{\epsilon_0 \epsilon_s}{L_D} \left(\because \frac{p_{n0}}{n_{n0}} \text{ can be ignored} \right). \quad (2-18)$$

In ideal MIS structure, the applied voltage will partly appear across the insulator and partly across the semiconductor. Thus,

$$V = V_I + \psi_s \quad (2-19)$$

where V_I is the potential across the insulator and is given by

$$V_I = E_I d = \frac{|Q_s| d}{\epsilon_0 \epsilon_I} \left(\equiv \frac{|Q_s|}{C_I} \right). \quad (2-20)$$

Finally, from substitution Eq. (2-17) for (2-15) and considering Eq. (2-19), ideal capacitance-voltage (C - V) curve is obtained, shown in **Fig. 2-3 line (a)**.

To measure the differential capacitance, small ac signal is superimposed with dc voltage. Here, the differential capacitance is the change of the total charge which corresponds to the change of applied voltage. And usually, the mechanism for getting minority carriers to and from the inversion layer is dominant for the generation-recombination via traps near the back-ohmic contact or those in the depletion region near the semiconductor surface (see **Fig. 2-4**), which means the minority carrier can not respond with a rapid ac signal. In case line (a) in **Fig. 2-3**, the frequency of the small ac signal is enough low for the minority carrier (holes) to respond, and the mean thickness of the depletion layer which contribute to C_D reduced and disappeared, then, the total capacitance recovered up to the insulator capacitance C_I . On the other hand, in case of line (b) in **Fig. 2-3**, the frequency of the small ac signal is enough high not to respond, and the majority carrier at the edge of the depletion layer (opposite site from insulator) move to cover the change of electric field, so the total capacitance value is still remaining at the low value and is gradually reducing, in spite of the existence of the inversion layer. In line (a) and (b), the position of the carrier to respond to the small ac signal differentiate the C - V behavior under inversion condition. Finally, when the rate of dc bias variation become higher than the generation-recombination velocity of minority carrier, the inversion layer itself can not be formed, and the depletion region continuously grows to cover the increase of the electric field. Under such a condition, the mean thickness of the depletion layer which contribute to C_D continue to increase, then the total capacitance reduce continuously.

The equivalent circuits under accumulation, depletion and inversion conditions are shown in **Fig. 2-1 (a-3), (b-3), (c-3 and 3')**, respectively. The difference between

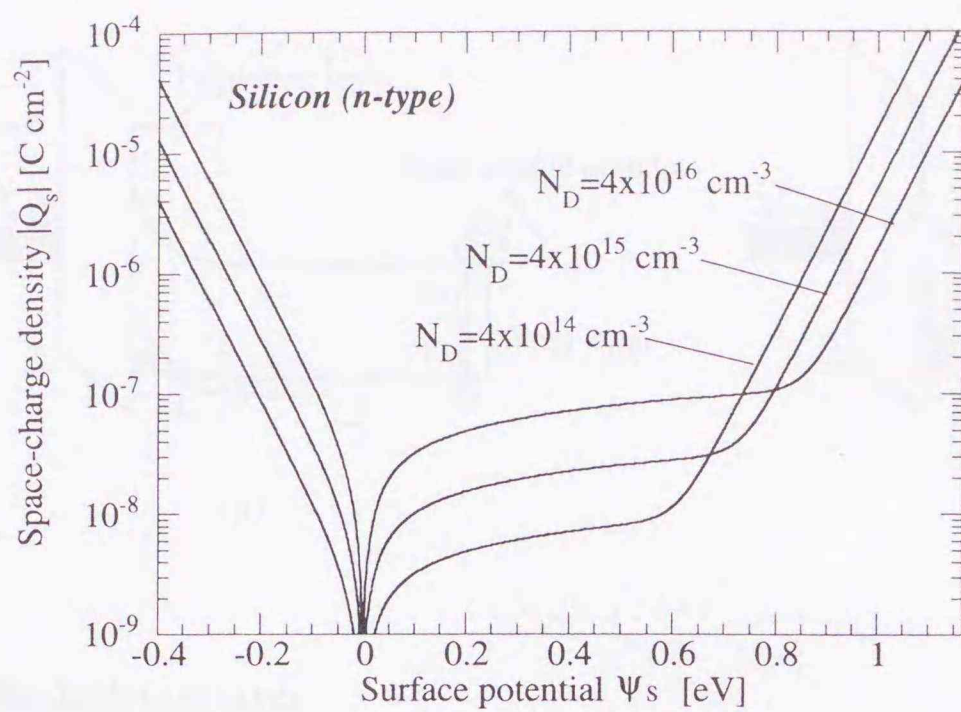


Fig. 2-2 Calculated space-charge density per unit area as a function of surface potential, ψ_s .

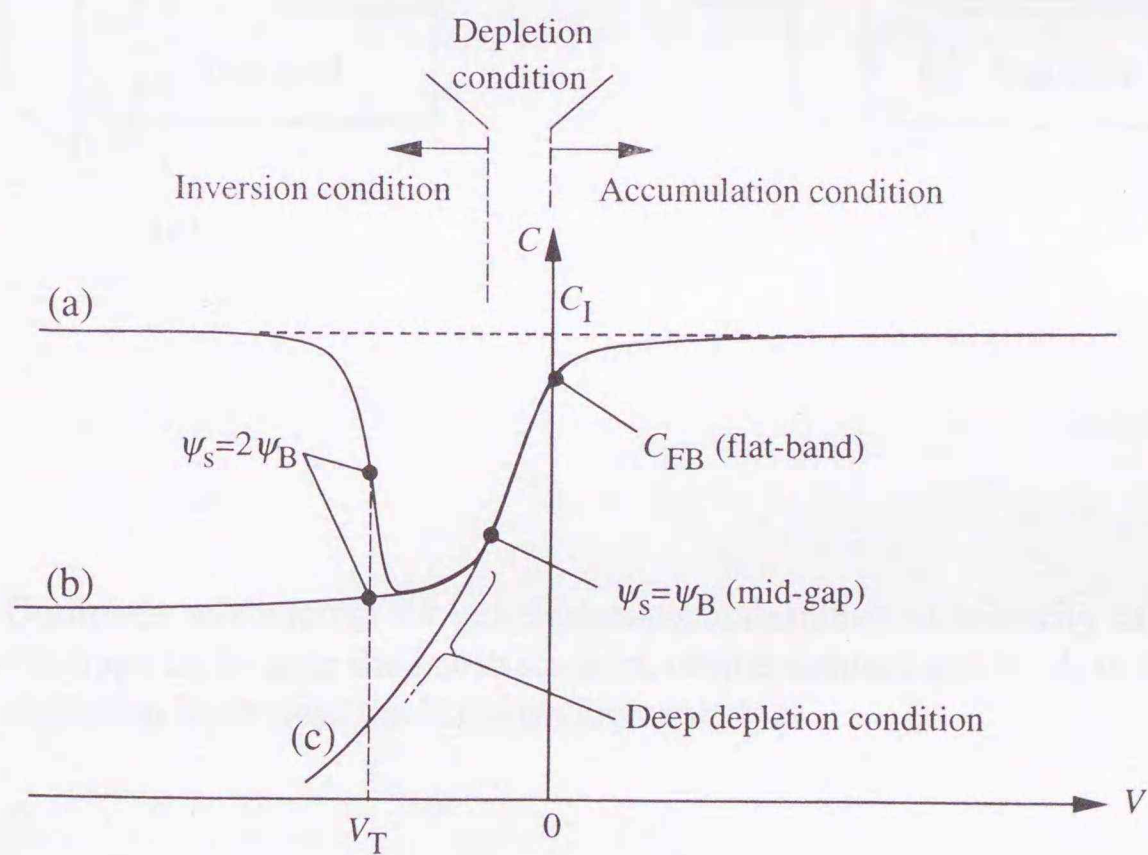
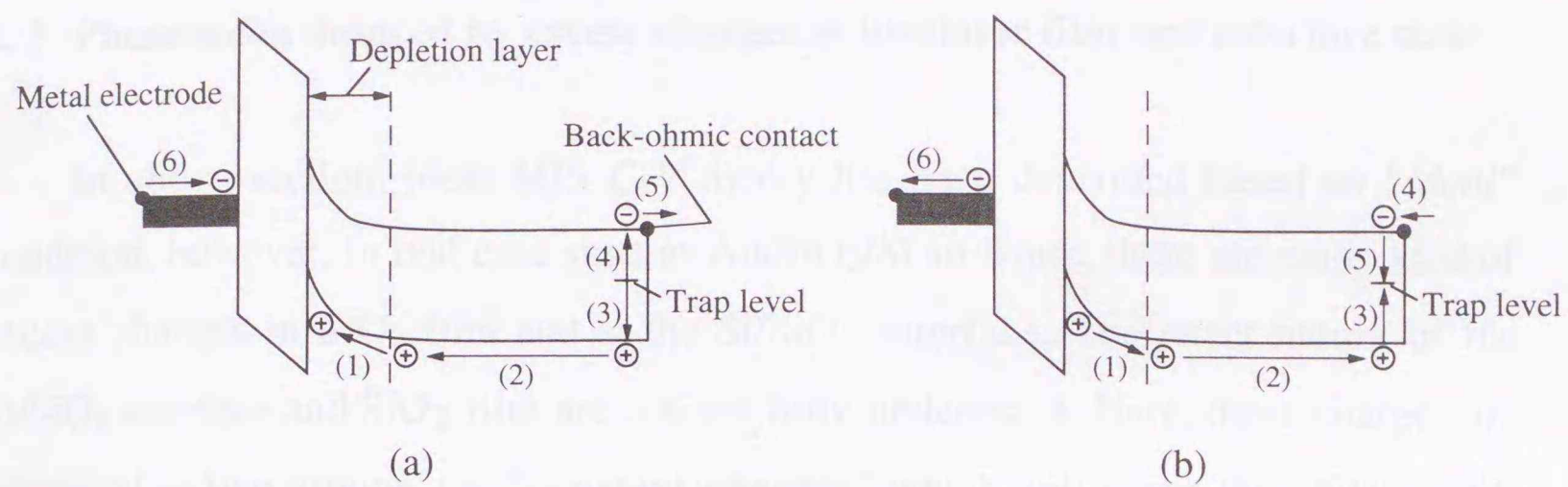


Fig.2-3 Ideal MIS C-V curves. (a) Low frequency curve. (b) High frequency curve. (c) Under pulse-mode biasing.

via traps near the substrate back-ohmic contact



via traps in the depletion layer

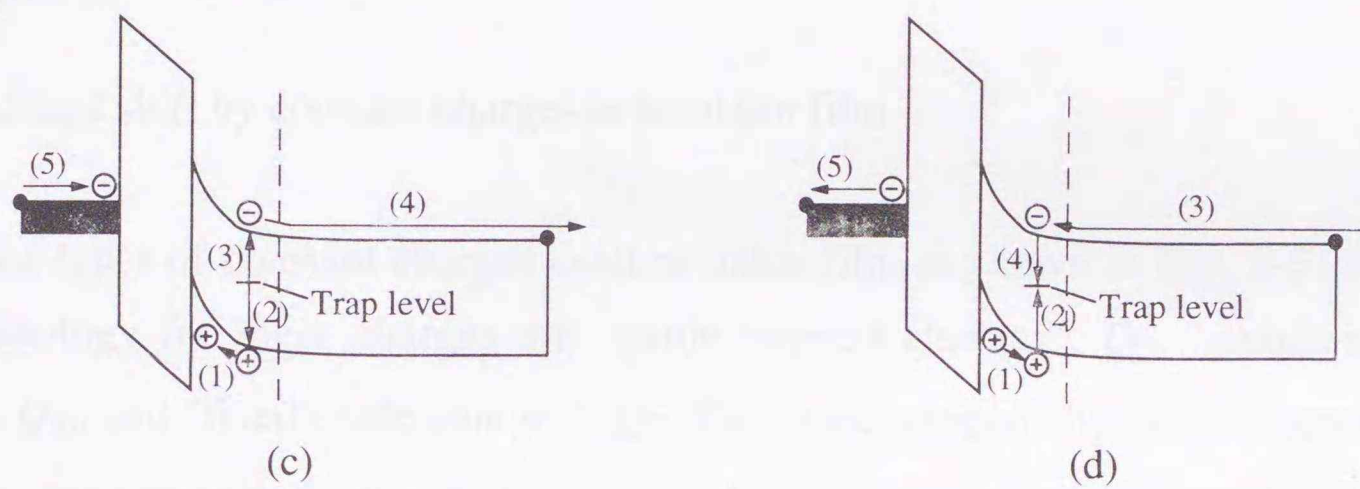


Fig. 2-4 Dominant mechanism for generation-recombination of minority carrier via traps (a, b) near the substrate back ohmic-contact and (c, d) in the depletion layer near the semiconductor surface.

low-frequency and high-frequency conditions are expressed in (c-3) and (c-3').

2.3 Phenomena induced by excess charges in insulator film and interface state

In above section, ideal MIS C-V theory has been described based on "ideal" condition, however, in real case such as Au/SiO₂/Si structure, there are many kind of excess charges in SiO₂ film and at the Si/SiO₂ interface. The exact nature of the Si/SiO₂ interface and SiO₂ film are not yet fully understood. Here, these charges are classified to two groups, i.e. "constant charges" which will cause the voltage shift and "variable charges" which will cause the Fermi-level pinning.

2.3.1 Voltage shift by constant charges in insulator film

Three types of constant charges exist in oxide film as shown in **Fig. 2-5**. Here, the terminology for these charges are "oxide trapped charges", Q_{ot} , "mobile ionic charges", Q_m , and "fixed oxide charges", Q_f . The oxide trapped charges are generally formed by, for example, x-ray radiation or hot-electron injection which cause negative or positive charges. The mobile ionic charges are such as sodium or potassium ions, which are mobile within the oxide layer under bias-temperature aging conditions. The fixed oxide charges are located at or near the Si/SiO₂ interface and usually possess positive charges. Here, the total of all constant charges are rewrote as "oxide charges", Q_o ,

$$Q_o = Q_{ot} + Q_m + Q_f. \quad (2-21)$$

The effect of oxide charges on electric field between metal plate and space charge region of semiconductor, and on C-V characteristics are shown in **Fig. 2-6**. For the ideal case ($Q_o=0$), to require charge neutrality, the same amount but opposite charges come from the ionized donor. However, in case $Q_o>0$, it needs lower bias voltage to form depletion layer or inversion layer compared to the ideal case (**Fig. 2-6**

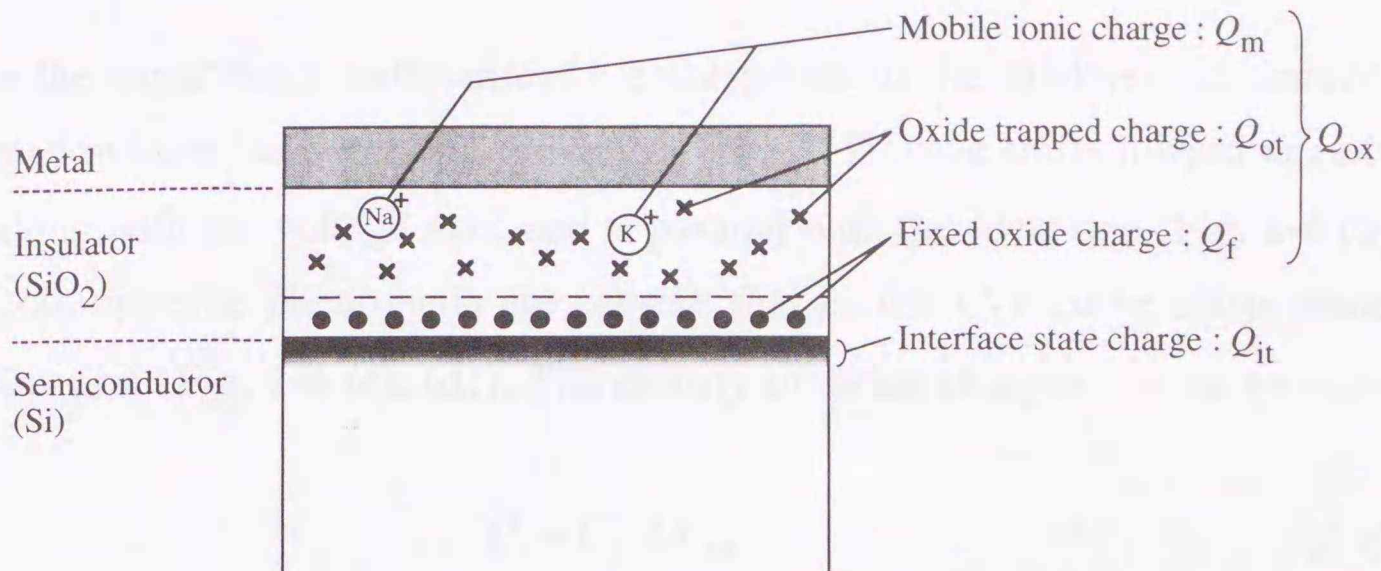


Fig. 2-5 Various kinds of charges in natural MIS structure.

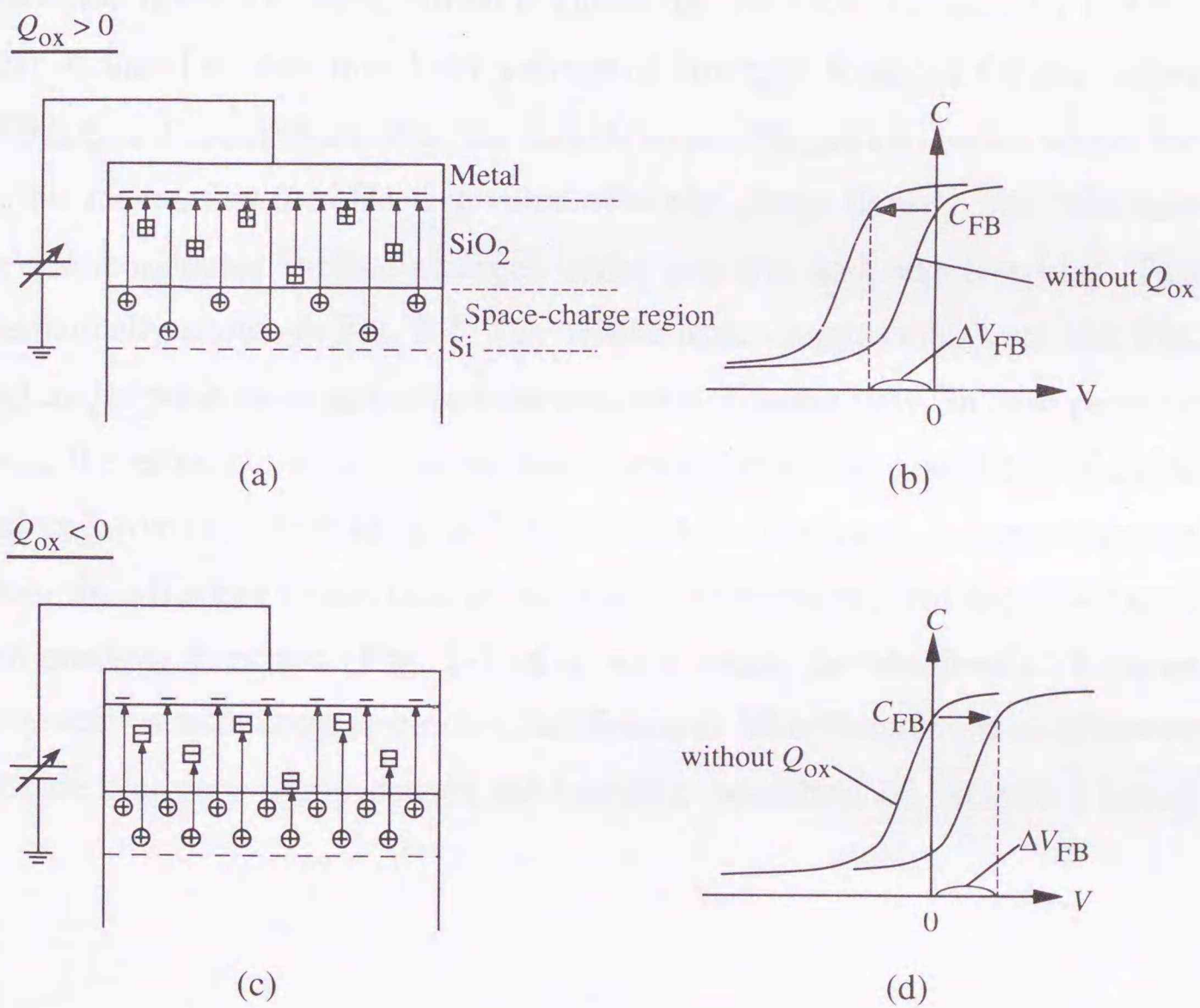


Fig. 2-6 Effect of oxide charges on electric field between metal plot and space charge region of semiconductor, and on $C-V$ characteristics. In case $Q_{ox} > 0$, it need much low voltage to eliminate the electric field from oxide charge, which leads the $C-V$ curve shift toward negative bias side (a, b). And in case $Q_{ox} < 0$, the space-charge region has been formed in advance, which leads the $C-V$ curve shift toward positive side..

(a)). Since the capacitance value directly corresponds to the thickness of semiconductor depletion layer, as described previously, the C - V curve shifts toward negative direction along with the voltage axis, and is parallel with the ideal one (**Fig. 2-6 (b)**). In case $Q_o < 0$, opposite phenomena are caused, that is, the C - V curve shifts toward positive direction (**Fig. 2-6 (c), (d)**). The density of oxide charges can be estimated by

$$Q_o = C_i \cdot \Delta V_{FB} \quad (2-22)$$

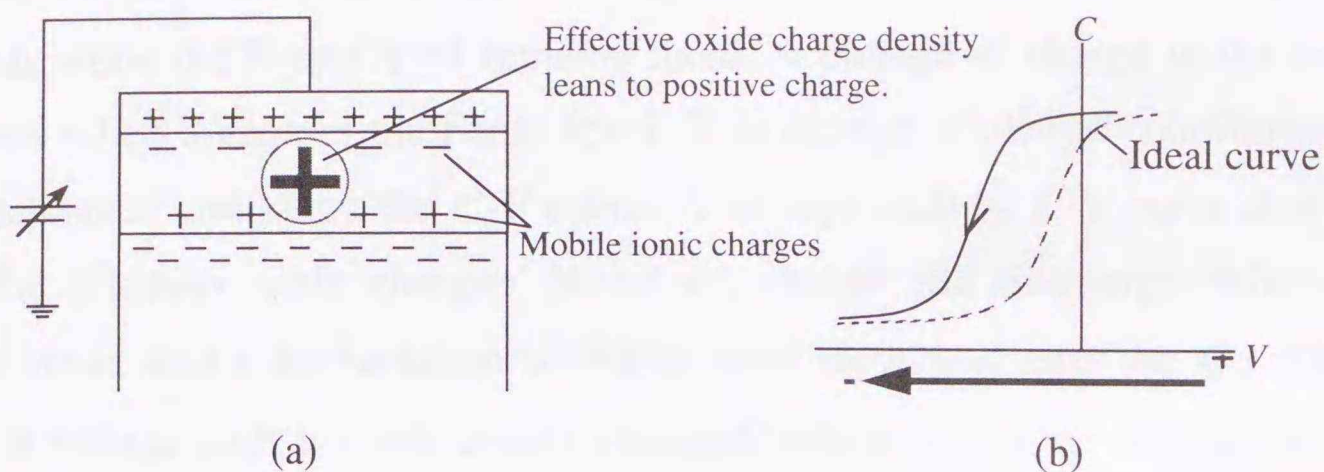
where ΔV_{FB} is the flat-band voltage shift as shown in **Fig. 2-6**.

The logic devices using MOSFET can work by changing the surface conduction type underneath the gate structure. The existence of oxide charges affects the voltage to form the inversion layer, which is called the threshold voltage, V_T (shown in **Fig. (2-3)**). Control of this threshold voltage is strongly required for the stable operation of MOSFET. And especially, the mobile ionic charges can move within the oxide layer, this means that the effective value of oxide charge density from the view point of the semiconductor surface changes under positive and negative bias. This effect is schematically shown in **Fig. 2-7**. The mobile ionic charges distribute like **Fig. 2-7 (a)** or **(c)** under positive or negative bias condition, respectively. In case positive bias condition, the effective oxide charge leans toward positive, and the C - V curve shifts toward negative direction (**Fig. 2-7 (b)**). On the other hand, in case negative bias condition, the effective oxide charge leans toward negative, and the C - V curve shifts toward positive direction (**Fig. 2-7 (d)**). As a result, the obtained C - V curve possesses a hysteresis with counter-clock-wise direction. This fluctuation of effective amount of oxide charge directly causes the unstable operation of MOSFET-based circuits.

2. 3. 2 Pinning of Fermi-level by variable interface state charges

Interface state charges, Q_{it} , exist at and near the Si/SiO₂ interface as shown in **Fig. 2-5**. In energy space, interface states exist within the forbidden gap mainly due to the interruption of the periodic lattice structure at the surface. The interface trap

Under positive bias condition.



Under negative bias condition.

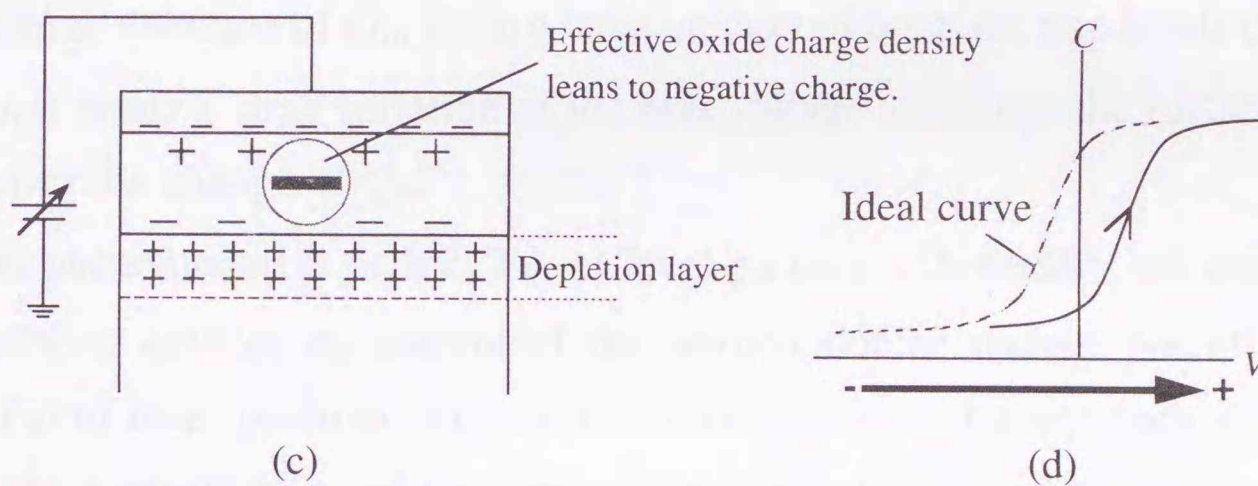


Fig. 2-7 Effect of mobile ionic charges under positive and negative bias conditions. The mobile ions change their position with applied bias voltage, and the effective density of oxide charge changes. Under positive bias condition, the oxide charge density leans to positive charge (a), and the C-V curve shifts toward negative direction (b). On the other hand, under negative bias condition, the oxide charge density leans to negative charge (c), and the C-V curve shifts toward positive direction (d).

includes two types of state, i.e. *acceptor type* and *donor type* traps. Acceptor type traps are negative when filled by electrons, and neutral when empty, whereas donor type traps are neutral when filled and positive when empty. Under applied bias condition, the interface-trap levels move up or down with the valence and conduction bands while the Fermi level remains fixed. A change of charge in the interface trap occurs when it crosses the Fermi level. This change of charge contributes to the MIS capacitance and alters the C - V curve. A voltage shift of C - V curve also occurs due to the interface state charges. However, charge and discharge behaviors of interface states make the variation of Fermi level slow, and alter the Q_{it} . Then the amount of voltage shift is continuously changed, which causes the stretch-out of C - V curve along with the voltage axis.

When very large amount of interface states exist, Fermi level shows almost no variation in response to the applied voltage. For, a small change of surface potential causes a large variation of Q_{it} , since a large amount of interface trap levels cross Fermi level. So, it needs a large variation of the bias voltage to change the surface potential and to cover the change of Q_{it} .

This phenomenon is called "Fermi level pinning". Generally, we can drive the semiconductor devices by control of the semiconductor surface potential, i.e. the surface Fermi level position. However, the existence of the interface state charges disturbs the controllability of the surface Fermi level position and causes the Fermi level pinning phenomenon, the theory for the semiconductor devices can not be applied. So, to understand and to characterize the density of the interface state charges are important. In section 2.4, the modeling of interface state is described, and in section 2.5 and 2.6, the characterization methods used in this study are explained.

2.4 Modeling of insulator-semiconductor interfaces based on the unified disorder-induced-gap-state (DIGS) model

The unified disorder-induced-gap-state (DIGS) model is firstly proposed by H. Hasegawa and H. Ohno in 1986⁸). This model is a advanced model of the surface

disorder model which is based on experimental results that the frequency dispersion of time constant for interface state is reflected in an exponential decrease in space. Using this model, insulator-semiconductor (I-S), metal-semiconductor (M-S) and semiconductor-semiconductor (S-S) interfaces can be discussed about Fermi level pinning phenomena and their energy positions.

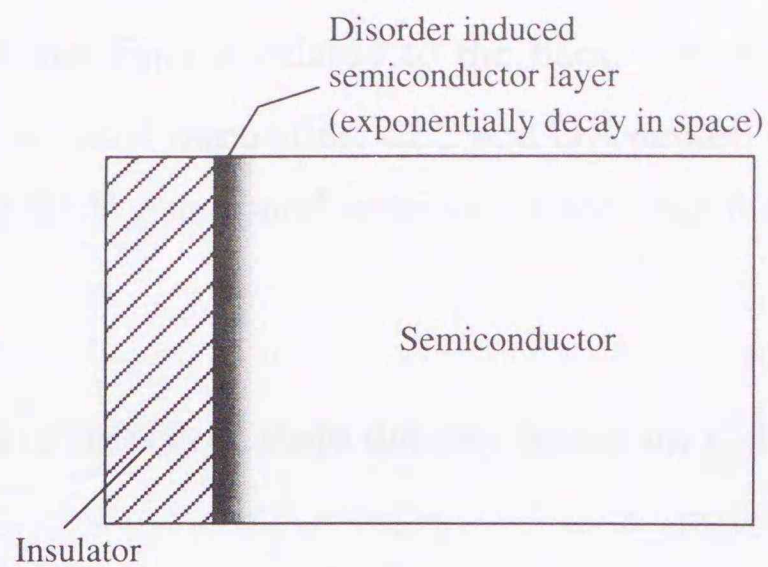
Deposition of metal or insulator or regrowth of semiconductor disturbs the crystalline perfection of the semiconductor. Since the interface irregularities such as lattice mismatch, introducing other materials, shift from the stoichiometry condition due to chemical reaction, point defects, stress and so on are exist, a disorder region which is composed disorder of bond length and bond angle is formed in the interface region as shown in **Fig. 2-8 (a)**. These give the incomplete separation of bonding state and anti-bonding state. As shown in **Fig. 2-8 (b)**, the distribution shape of interface state density in the energy gap is continuous U-shaped in the unified DIGS model, and the DIGS density depends on the degree of disorder. The DIGS density spectrum consists of bonding (donor-like) and anti-bonding (acceptor-like) states, and the characteristic energy E_{HO} can be interpreted as the Fermi energy location of the DIGS spectrum which is the boundary between two of states where charge neutrality is achieved.

From a simple tight-binding picture, the location of the Fermi level of the DIGS spectrum, E_{HO} , can be given by

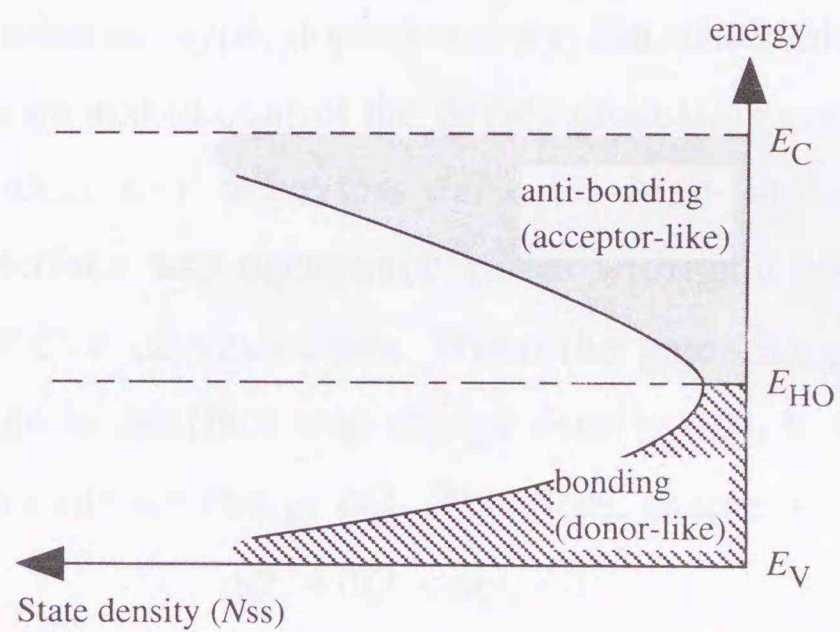
$$E_{HO} = \frac{(\epsilon_s + \epsilon_p)_{av.}}{4} + \Delta U \quad (2-23)$$

where ϵ_s and ϵ_p are atomic term energies and the average is to be taken over constituent cations and anions, and ΔU is the correction for electron-electron interaction. The energy position of E_{HO} is independent of whether the structure is ordered or disordered, and lies approximately at 5.0 eV from vacuum level.

The Schottky barrier is formed on M-S interface because the surface Fermi level is pinned at the electrical neutrality point (E_{HO}) of DIGS with a density higher than that of I-S interface. This unified DIGS model explains that the Schottky barrier height is determined by balance between metal workfunction and interface state



(a)



(b)

Fig. 2-8 (a) Disordered layer formed at semiconductor interface and (b) U-shaped DIGS continuum due to incompleteness of energy band separation caused by disorder.

charge which is generated owing to a slight shift of Fermi level from E_{HO} .

It has been found that E_{HO} is related to the band-lineup of heterojunction and energy level of transition metal impurities, EL2 and DX center. **Figure 2-9** shows the relationship concerning III-V compound semiconductors and their alloys.

2.5 Characterization of interface state density based on C - V measurement

For the determination of the interface state density, capacitance-voltage (C - V) method is one of simple methods and gives the accurate and quantitative informations. Furthermore, C - V method is suitable to determine the device-oriented properties such as conduction type, doping density, flat-band voltage shift, which are very important to design and to control the device processing conditions.

Two types of ideal C - V behaviors exist, i.e. high- and low-frequency C - V curves. Since the interface trap occupancy varies with gate bias, V_G , as described above, stretch out of C - V curves occurs. When the gate charge is changed by an amount dQ_G , a change in interface trap charge density dQ_{it} is also occurs together with the semiconductor surface charge dQ_s . Therefore, charge balance satisfies

$$dQ_G + dQ_s + dQ_{it} = 0. \quad (2-24)$$

The additional change in charge density dQ_{it} requires the change in dQ_s less. Thus the change in band bending is less than that of ideal case. Consequently, to change the surface condition from accumulation to inversion requires a larger range of gate charge variation. Thus the C - V curve is stretched out along with the gate bias axis.

From Gauss's law, a quantitative treatment of this stretch out can be obtained,

$$C_I \cdot (V_G - \psi_s) = -Q_{it}(\psi_s) - Q_s(\psi_s), \quad (2-25)$$

or

$$C_I \cdot dV_G = [C_I + C_{it}(\psi_s) + C_D(\psi_s)] \cdot d\psi_s \quad (2-26)$$

where C_{it} and C_s are differential capacitances for interface trap charges and semiconductor surface, respectively. The density of interface state, D_{it} , can be written by

$$C_{it}(\psi_s) \approx qD_{it}(\phi_s). \quad (2-27)$$

2. 5. 1 High-frequency method (Terman's method)⁷⁾

In case the frequency of small ac signal is enough high so that interface state do not respond, the charges in interface traps can not contribute as capacitance to the high-frequency C - V curve. Here, "high-frequency" means a frequency sufficiently high that neither interface traps nor minority carriers follow the small ac signal. Although interface trap charges do not follow the ac signal in a high-frequency C - V measurement, they do follow very slow changes in gate bias which is swept from accumulation to inversion. So, existence of interface traps cause the stretch out of a high-frequency C - V curve, because interface trap occupancy must be changed in addition to changing depletion layer charge.

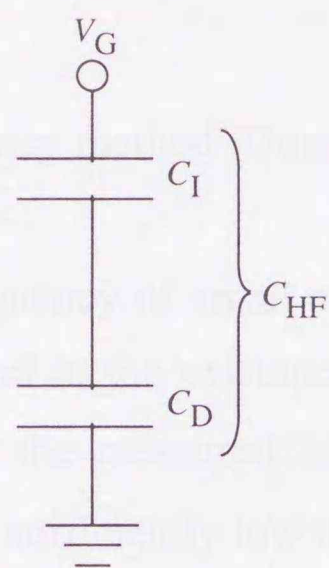
The equivalent circuit of high-frequency MIS capacitor is shown in **Fig. 2-10 (a)**, the series connection of the insulator capacitance, C_I , and the semiconductor depletion layer capacitance, C_s . Here, this equivalent circuit is the same as that of the ideal MIS structure as shown in **Fig. 2-1 (b-3)**. Therefore, measured C_{HF} will be the same as the ideal if band bending is the same. By knowing Ψ_s vs. C_{HF} in the ideal case and measuring V_G vs. the same C_{HF} , we can construct a Ψ_s vs. V_G relationship. **Fig. 2-11** shows a comparison of $C_{HF}(\Psi_s)$ vs. Ψ_s with C_{HF} vs. V_G . Thus the $d\Psi_s/dV_G$ is derived from the slope of Ψ_s - V_G plot, and the $C_{it}(\Psi_s)$ can be determined from Eq. (2-26) as

$$C_{it}(\Psi_s) = C_I \cdot \left[\left(\frac{d\Psi_s}{dV_G} \right)^{-1} - 1 \right] - C_D(\Psi_s). \quad (2-28)$$

Once C_{it} is found from Eq. (2-28), density of interface state D_{it} is given using Eq. (2-27).

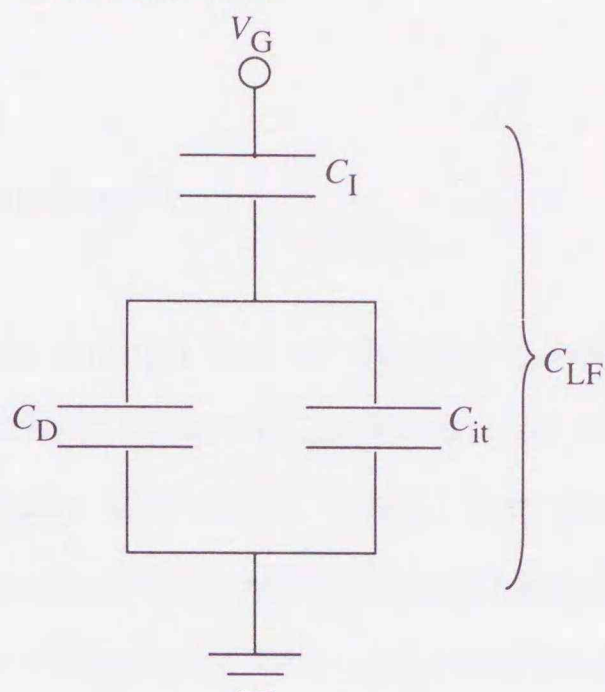
The high-frequency C - V method was developed by Terman, so this is, sometimes, called "Terman's method". The principle of ultrahigh-vacuum (UHV) contactless capacitance-voltage (C - V) measurement technique mainly used in this study is based on this high-frequency C - V method (Terman's method). The details of the UHV

High-frequency



(a)

Low-frequency



(b)

Fig. 2-10 Equivalent circuits for (a) high-frequency and (b) low-frequency.

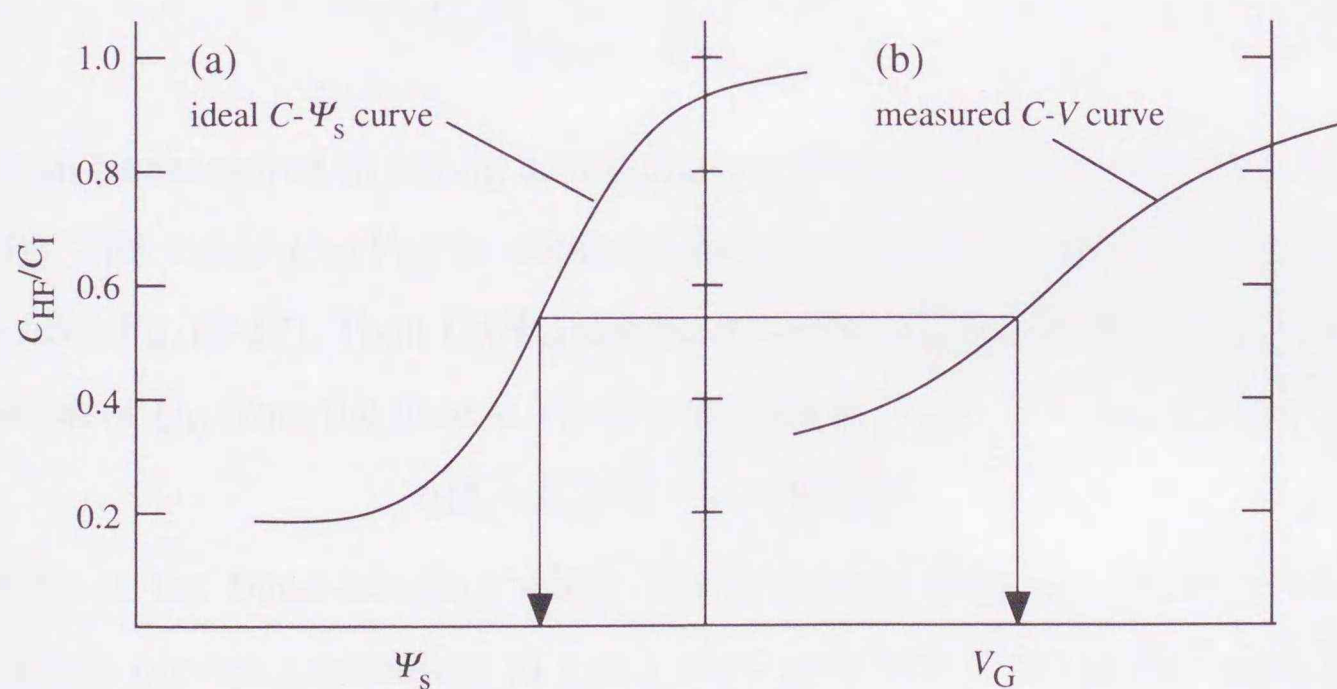


Fig. 2-11 The principle of high-frequency C - V method. (a) ideal C - Ψ_s curve and (b) measured C - V curve. By comparing the ideal C - Ψ_s and measured C - V , V - Ψ_s curve can be obtained.

contactless C - V technique is described later.

2. 5. 2 Low-frequency method (Quasi-static method)⁷⁾

In case a frequency of small ac signal is enough low so that the interface trap charges can respond it, the existence of interface state will contribute an additional capacitance C_{it} to the measured low-frequency C - V curve. Here, "low-frequency" means a frequency sufficiently low that all interface traps and minority carriers follow the small ac signal. Similarly, the measured low-frequency C - V curve will be stretched out along the gate voltage axis, because the interface traps follow changes in gate bias.

The equivalent circuit of low-frequency MIS capacitor is shown in **Fig. 2-10 (b)**, and the total capacitance value C_{LF} is written as

$$\frac{1}{C_{LF}} = \frac{1}{C_I} + \frac{1}{C_D + C_{it}}. \quad (2-29)$$

Solving (2-29) for C_{it} yields

$$C_{it} = \left[\frac{1}{C_{LF}} - \frac{1}{C_I} \right]^{-1} - C_D. \quad (2-30)$$

Here, C_I can be measured in strong accumulation. We need $C_D(V_G)$ to obtain C_{it} from Eq. (2-30). The value $C_D(V_G)$ is obtained by calculation. At first, $C_D(\Psi_s)$ can be obtained from Eq. (2-17). Then $C_s(\Psi_s)$ can be related to $C_s(V_G)$ if Ψ_s vs. V_G is known.

The variation of Q_G from the time at $V_G=0$ is written as

$$\Delta Q_G = C_I [V_G - \psi_s + \psi(0)] \quad (2-31)$$

where $\psi(0)$ is the band-bending when $V_G=0$. Rather than use an ac method, in practice it has proven convenient to use a slow gate bias ramp and to measure the resulting displacement current with an electrometer. Usually, "a slow gate bias ramp" means a very small step variation of gate bias, and it is necessary to wait enough time responding all interface states with the small variation of gate bias. Thus, this method is, sometimes, called "quasi-static method". Differentiating Eq. (2-31) with respect to

V_G yields

$$\frac{d\psi_s}{dV_G} = 1 - \frac{C_{LF}}{C_I} \quad (2-32)$$

where $C_{LF} = dQ_G/dV_G$. Integrating Eq. (2-32) and considering $\Psi_s(V_{FB}) = 0$ yield

$$\psi_s(V_G) = V_G - V_{FB} - \frac{1}{C_I} [C_{LF}(V_G) - C_{LF}(V_{FB})] \quad (2-33)$$

where $C_{LF}(V_G)$ is measured under low-frequency condition and $C_{LF}(V_{FB})$ can be calculated by Eq. (2-18). Now, V_{FB} must be determined using other techniques such as Q - V method or high-frequency C - V method. Here, the details are omitted.

2. 6 Other characterization methods used in this work

To understand and control of the insulator-semiconductor interface for further advance the CMOS technology to its ultimate scaling limits as well as to develop new nano-scale quantum effect devices, investigation of the nature of semiconductor surfaces/interfaces based on not only electronic analysis but also chemical, optical and structural analyses become important. In this work, X-ray photoelectron spectroscopy (XPS), photoluminescence surface state spectroscopy (PLS³) and atomic force microscopy (AFM) are used for the chemical, optical and surface structural analyses, respectively. The details are written in turn.

2. 6. 1 X-ray photoelectron spectroscopy (XPS)

A photoelectron spectroscopy technique is one of standard and basic method for the analysis for semiconductor surfaces, and this technique has been highly developed for long time. A x-ray or ultra-violet (UV) ray are generally used to emit photoelectrons, the former and the latter are called "x-ray photoelectron spectroscopy (XPS)" and "ultra-violet-ray photoelectron spectroscopy (UPS)", respectively. More

generally, these are, including auger-electron spectroscopy (AES), called "electron spectroscopy for chemical analysis (ESCA)". The photon energy of x-ray is much higher than that of UV-ray, enough to excite electrons in core-levels which are not contributed to the binding but include the information of the binding conditions. So, XPS technique is one of powerful characterization method of semiconductor surfaces and semiconductor-insulator interfaces.

1) Principle of XPS

A basic principle of XPS measurement is to apply a spectroscopic analyses on photoelectrons which are emitted from a sample surface by irradiating x-ray. Generally, Mg $K\alpha$ soft x-ray (photon energy of 1253.6 eV) or Al $K\alpha$ soft x-ray (1486.6 eV) is used. These photons have limited penetrating depth of the order of micro-meter in solid, and have enough energy to emit core-level electrons by the photoelectric effect. The emitted electron energy has the kinetic energy E_K given by

$$E_K = h\nu - E_B - q\zeta_s \quad (2-34)$$

where $h\nu$ is the photon energy of x-ray, E_B is the electron binding energy of the atomic orbital which the electron emitted and $q\zeta_s$ is the spectrometer work-function. The energy relationship is illustrated in **Fig. 2-12**. The Fermi level corresponds to zero binding energy by definition. The spin-degenerated p , d and f levels are observed due to spin-orbital interaction. In addition to the photoelectrons, Auger electrons are emitted due to relaxation of energetic ions left after photo-emission.

Interactions of the electron and the photon occurs in the range of the order of micro-meters, however, photoelectrons without energy loss can be emitted in the range of the order of a few tens angstroms. The electrons with energy loss can not form a peak-shape spectra. In addition, the emitted electrons with inelastic process also cause anti-peak-shape spectra. These are called "*background*" spectra.

The photoelectric effect occurs by x-ray irradiation. Usually, the x-ray possesses harmonics which cause electron emission with high kinetic energy. These electrons are counted with low binding energy, and form "*satellite peaks*". Furthermore, if the x-ray source has impurities, these undesirable materials also cause the x-ray emissions which have different wave-length. The emission of electrons occur by photons and

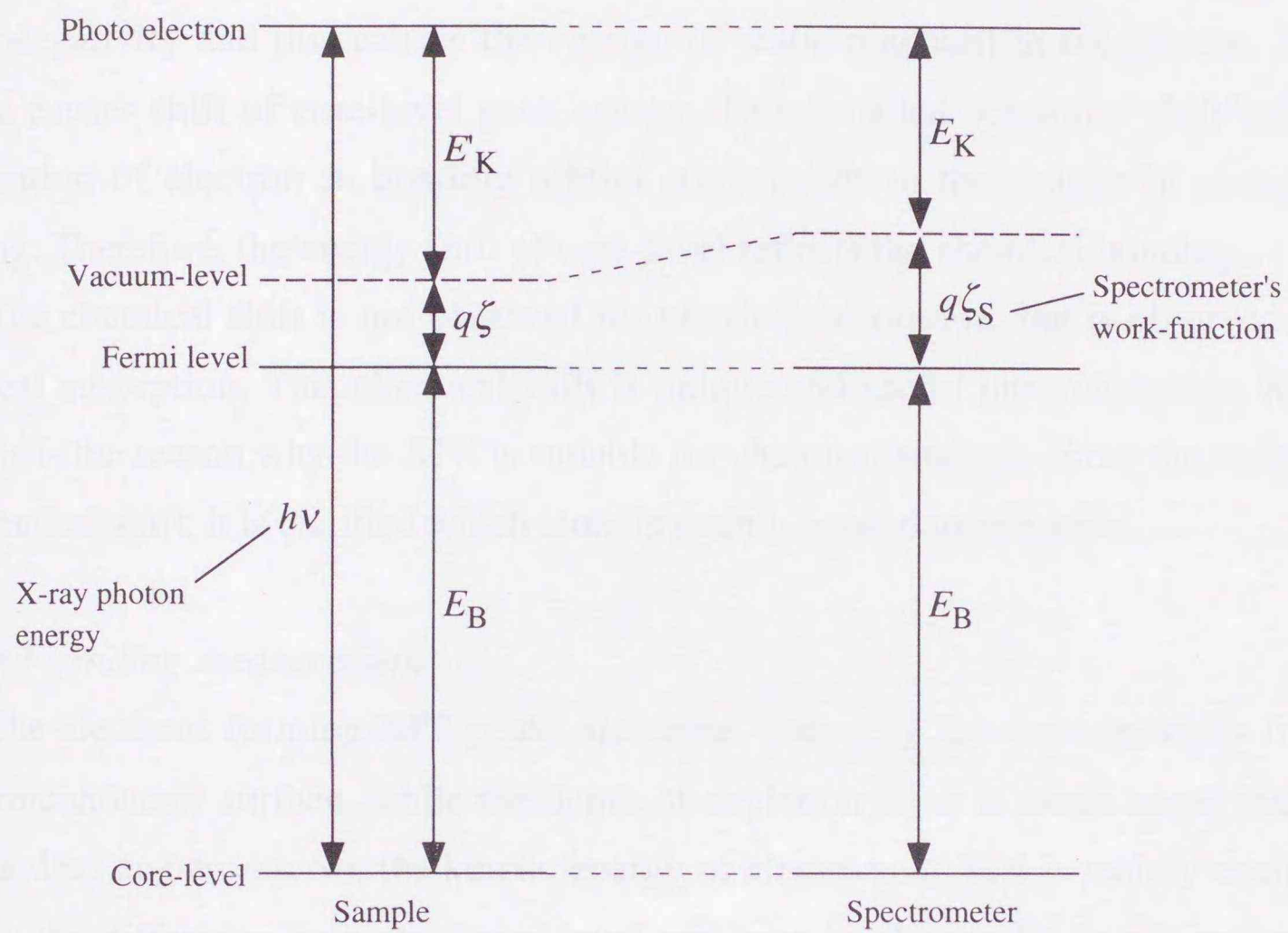


Fig. 2-12 Energy diagram of sample and spectrometer in XPS.

form "ghost peaks".

2) Chemical shift

Electron confined in each core-level does not affect on bond between atoms. On the other hand, electrons in bonding orbital moves toward atoms having large electronegativity and this causes the change of static potential in the system. This change causes shift of core-level peak energy. This is called "chemical shift". Such reformation of electron in bonding orbital corresponds to the change in chemical bonding. Therefore, the energy shift of core-level reflects the chemical bonding.

The chemical shift is not observed for physical adsorption, but is observed for chemical adsorption. This chemical shift is unique and useful phenomenon in XPS, and this is the reason why the XPS is suitable for chemical analysis. From the value of the chemical shift, it is clarified which atom is mainly bonded to one atom.

3) Band-bending measurement

The electrons forming XPS peaks are come from only few ten angstroms from the semiconductor surface, while the depth of depletion layer is much larger than a few hundred angstroms. So, the kinetic energy of electrons in XPS is mainly contributed by the difference between Fermi level and core-level energies just at and near the surface. When the surface potential changed (band bends upward), the peak position in XPS shifts (toward lower energy direction). As shown in **Fig. 2-13**, the band-bending, $q\psi_s$, can be obtained by

$$\begin{aligned} q\psi_s &= E_{B_measured} - E_{B_bulk} \\ &= E_{B_measured} - (E_F - E_V) - (E_V - E_{Si2p}) \end{aligned} \quad (2-35)$$

where $E_{B_measured}$ is the measured peak position of Si_{2p} XPS spectra and E_{B_bulk} is the energy difference between E_F and E_{Si2p} . Here, the Si is used as an example. The energy difference between E_F and E_V can be calculated by a doping density, and $E_V - E_{Si2p}$ must be determined theoretically or experimentally. In case of Si, Himpsel et al. determined this value using very high doped n- and p-type Si substrates which positions of Fermi level are regarded as the same positions as those of E_C or E_V . Thus

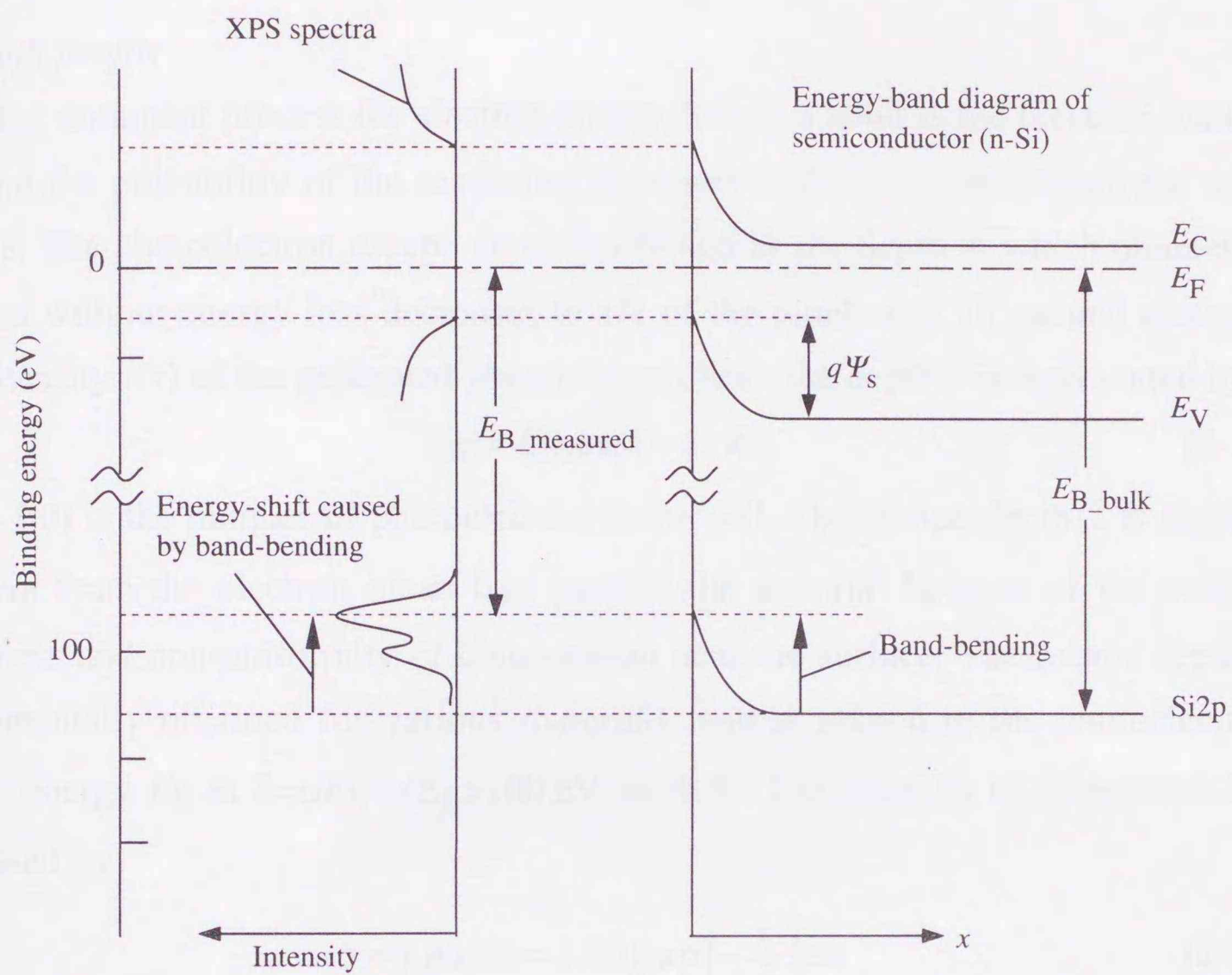


Fig. 2-13 The principle of band-bending measurement by XPS method. The core-levels bend with the E_C and E_V . The XPS spectra can detect those bindings.

the value of $(E_V - E_{Si2p})$ is determined 98.78 eV in Si. Thus, by using this value and considering the carrier density, the value of band-bending can be estimated.

4) Depth profile

The dominant process for electron energy loss in a solid is the inelastic scattering, and the probability of the scattering increases with the distance from the solid surface. The photoelectron escape depth is defined as the depth at which number of electron without energy loss decreases to $1/e$ of the number of all excited electron. The intensity $I(x)$ of the generated photoelectron from the depth x is represented by

$$I(x) = I(0)\exp(-x/\lambda) \quad (2-36)$$

where $I(0)$ is the number of photoelectron from $x=0$. The escape depth λ is slightly different from the electron mean free path in the material because of the surface roughness and non-uniformity of composition near the surface. The escape depth is experimentally obtained for various materials, and is related to the photoelectron kinetic energy E_K as $\lambda = \alpha E_K^m$ ($E_K > 100$ eV, $m \approx 0.5$). The intensity of a spectrum S is expressed by

$$S = \int_0^d I(x)dx = \int_0^d I(0)\exp\left(-\frac{x}{\lambda}\right)dx \quad (2-37)$$

where d is the thickness of outer layer (**Fig. 2-14**). Comparing S from the inner and outer layers, the thickness d can be calculated by

$$\frac{S_B}{S_A} = \frac{I_B(0)\lambda_B [1 - \exp(-d/\lambda_B)]}{I_A(0)\lambda_A \exp(-d/\lambda_A)} \quad (2-38)$$

where S_A and S_B , $I_A(0)$ and $I_B(0)$ are measured peak intensities and numbers of photoelectrons from $x=0$ for inner and outer layers, respectively. In case same element composes both inner and outer layer, i.e. $I_B(0)=I_A(0)$ and $\lambda_A=\lambda_B (= \lambda)$, d is given by

$$d = \lambda \ln \left(1 + \frac{S_B}{S_A} \right). \quad (2-39)$$

The angle between the sample surface and the axis of the spectrometers θ , which is called the photoelectron exit angle, determines the effective escape depth $\lambda \sin \theta$.

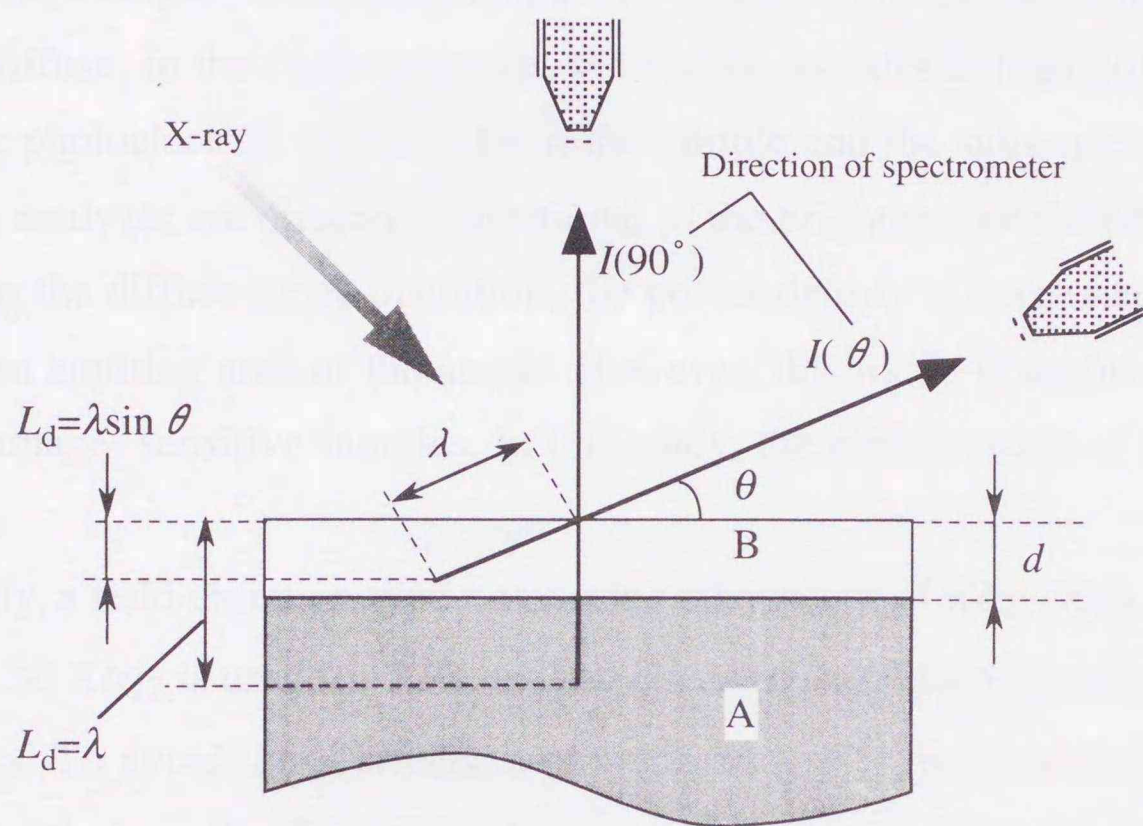


Fig. 2-14 Angle resolved analysis in XPS.

5) Apparatus of XPS

Figure 15 shows the schematic diagram of XPS measurement system including x-ray source, monochromator, analyzer, manipulator...

In this study, Al is used as an x-ray source. The acceleration energy is 14 kV. This system has a single static aluminum anode designed for operation in two modes, focussed or diffuse. In the focussed mode, the source operates at high power density. The resulting photoelectron emission from the sample and the subsequent count rate in the energy analyzer are directly proportional to the brightness of the anode. On the other hand, in the diffuse mode operation, the power density is decreased by enlarging the photon emitting area of the anode. However, this mode is useful for analysis of charge- damage- sensitive samples. In this study, the diffuse mode of operation is mainly used.

Generally, a field-emission-type x-ray using Al consists of $K\alpha_{12}$, $K\alpha_3$, $K\alpha_4...K\beta...$. In this study, Al $K\alpha_{12}$ is used for XPS, and others cause confusion in analysis, such as satellite peaks. To avoid these effects, a monochromator is mounted between the x-ray source and the sample. This monochromator provides an intense x-ray flux with monochromatic x-ray energy distribution and is based on a 500 mm Rowland circle geometry for high x-ray energy dispersion. This x-ray energy dispersion eliminates the $K\alpha_3$, $K\alpha_4...K\beta$ x-ray lines and the Al Bremsstrahlung radiation background and narrows the Al $K\alpha_{12}$ line to approximately 0.2 eV full-width at half-maximum (FWHM). This narrow line allows core- and valence-band spectra to be acquired with high energy resolution of the photoemission peaks and without x-ray satellite-induced photoemission peak overlaps.

Figure 2-16 schematically shows the spherical capacitor analyzer with an input lens. The input lens accepts electrons originating at the sample surface, retards them to the kinetic energy passed by the analyzer, and focuses them on to the analyzer entrance slit. The analyzer contains two concentric hemispherical electrodes which are biased so that charged particles (electrons) of a selected energy follow nearly circular trajectories and are focused at the analyzer's exit slit. Energy selection occurs in the region between the two hemispherical electrodes. To ensure that the trajecto-

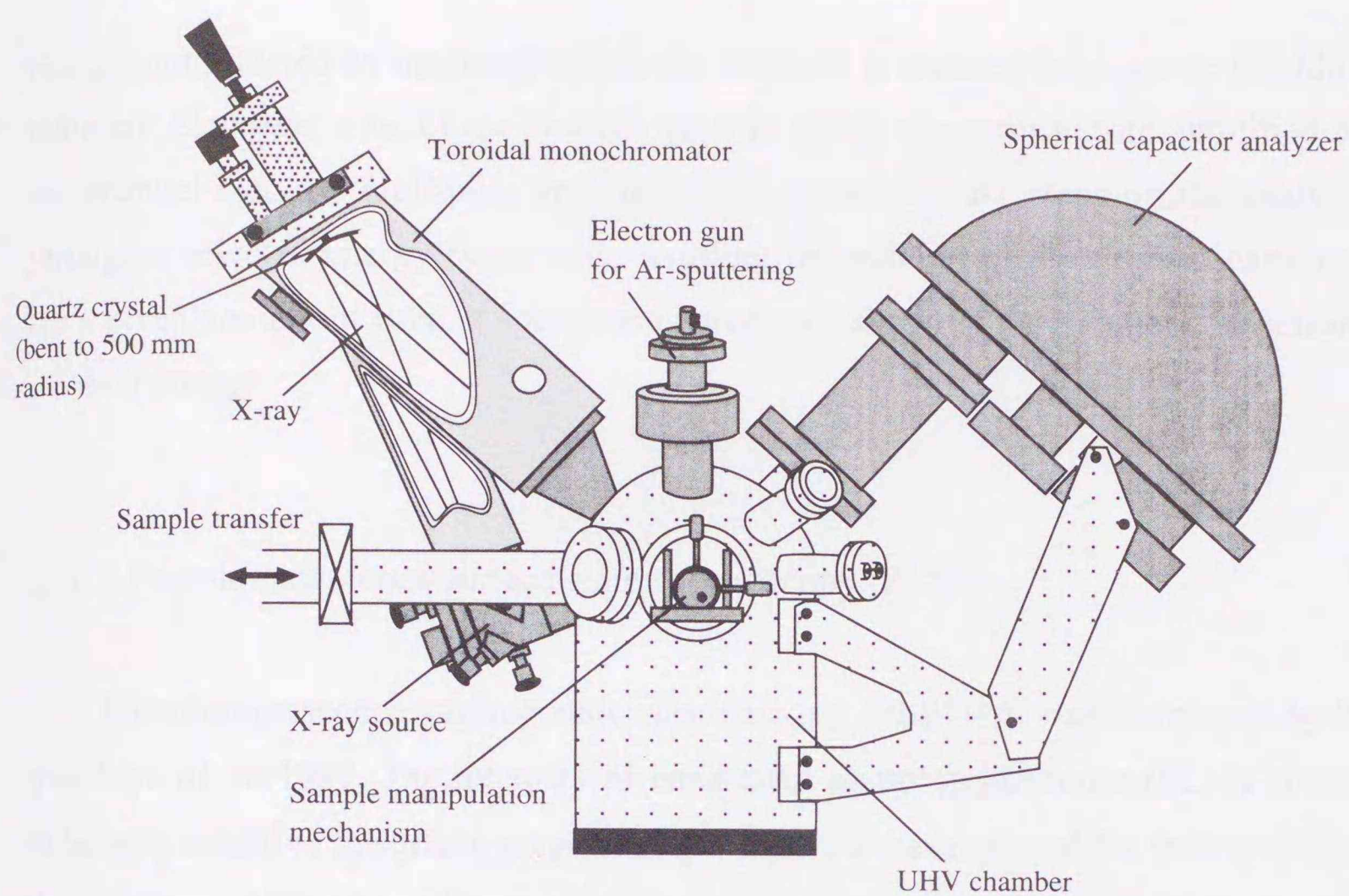


Fig. 2-15 Schematic diagram of XPS chamber used in this study.

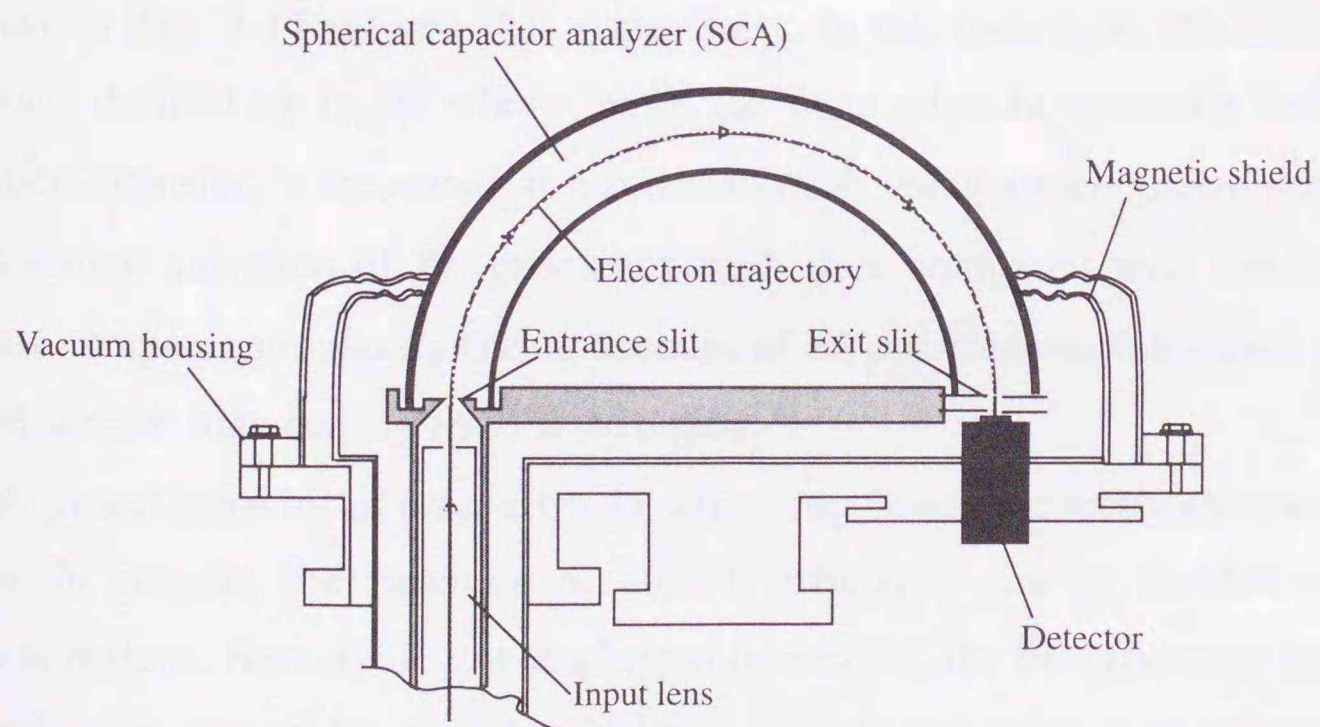


Fig. 2-16 A schematic view of spherical capacitor analyzer.

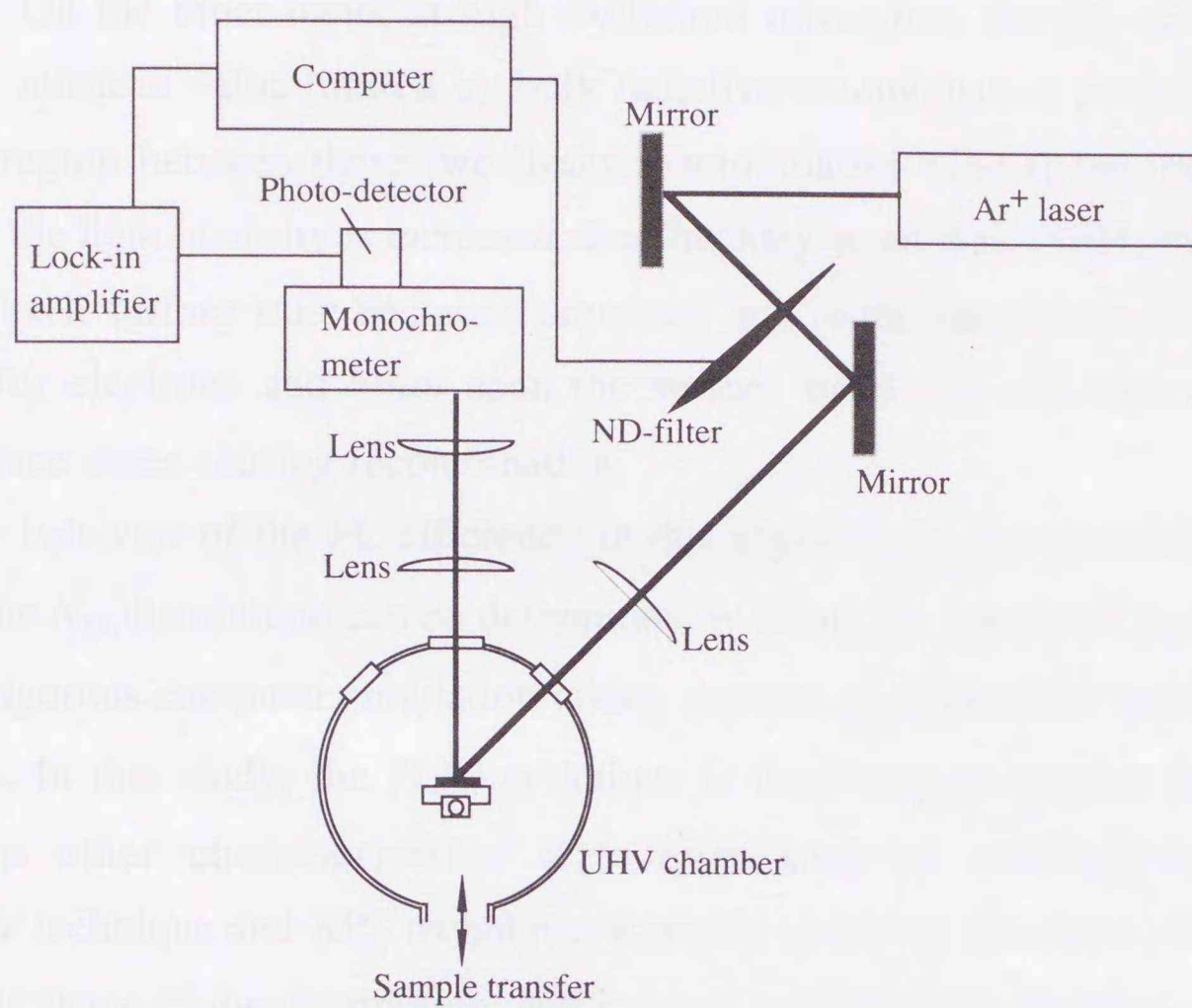
ries are not affected by magnetic fields, the analyzer is encased in magnetic shielding material. Electrons which pass through the exit slit of the analyzer are amplified by the channel electron multiplier and individually counted. By stepping the analyzer through a selected energy range and recording the number of electrons at each step for a given amount of time, a spectrum is produced showing the number of electrons vs. their energy.

2. 6. 2 Photoluminescence surface state spectroscopy (PLS³)

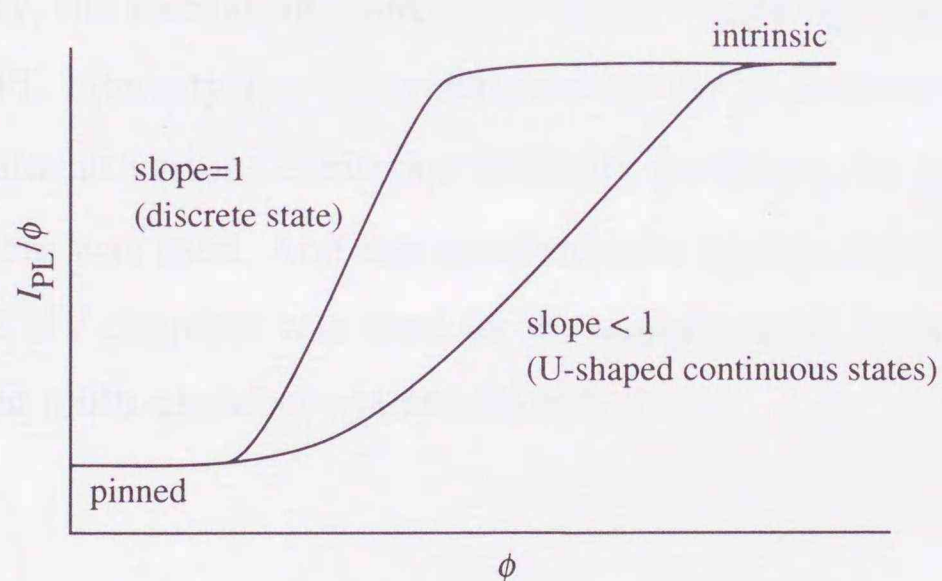
Photoluminescence surface state spectroscopy (PLS³)³⁻⁵ was developed by T. Saitoh *et. al.* in 1991. The intensity of band-edge photoluminescence (PL) is known to be very sensitive to surface properties. However, it was not used for their quantitative assessment. The photoluminescence surface state spectroscopy (PLS³) technique is a novel surface characterization technique intended for quantitative assessment of the surface state density properties of free and passivated surfaces in a contactless fashion.

The experimental setup and the principle of the PLS³ technique are schematically shown in **Fig. 2-17 (a)** and **(b)**, respectively. In this technique, the band-edge PL efficiency defined by I_{PL}/ϕ , where I_{PL} is the band-edge PL intensity and ϕ is the excitation intensity, is measured as a function of ϕ , using an automated setup. Then, the measured variation of PL efficiency with ϕ is compared with the result of a rigorous computer simulation taking account of all possible recombination processes and the surface state density (N_{ss}) distribution.

A typical behavior of band-edge PL efficiency is schematically shown in **Fig. 2-17 (b)**. In general, the variation of the PL efficiency can be divided into three different regions. Namely, at low excitation intensities, the PL efficiency takes a low constant value caused by a relatively large surface recombination velocity due to Fermi level pinning. In high quality Si and GaAs single crystals, the bulk recombination is of little importance. The value of the PL efficiency in this region is primarily determined by the pinning position of the surface Fermi level and the density of



(a)



(b)

Fig. 2-17 (a) Experimental setup of the PLS³ technique used in this study. (b) Schematic illustration of typical behavior of band-edge PL efficiency.

surface states. On the other hand, at high excitation intensities, the PL efficiency approaches an intrinsic value limited by bulk radiative recombination processes. In the transition region between these two limits, photoinduced band flattening takes place. Here, as the light intensity is increased, the Shockley-Read-Hall (SRH) recombination rate of each surface state becomes saturated, and at the same time, the quasi Fermi levels for electrons and holes scan the surface band gap and increase the number of surface states causing recombination.

Thus, the behavior of the PL efficiency in this region strongly reflects the N_{ss} distribution. The N_{ss} distribution can be determined by fitting the measured I_{PL}/ϕ with the results of rigorous computer simulation taking account of all possible recombination processes. In this study, the PLS³ technique is used only to support the data obtained from other characterization techniques such as ultrahigh-vacuum contactless $C-V$ technique and XPS technique. Roughly speaking, the slope of the PL efficiency gives shape of the distribution, and is equal to unity for a discrete distribution due to complete saturation of the SRH process. It is less steep for U-shaped continuous distribution.

In this study, the excitation source was an Ar⁺ laser light with a wavelength of 514.5 nm. The PL intensity I_{PL} was measured by the photodetector with the use of the monochromator at various excitation intensity ϕ changed by an ND-filter. A lock-in amplifier system was used. And this measurement system was fully controlled by a computer. The UHV chamber was used for the sample room, which can be connected to the UHV-based multi-chamber-system described later.

2. 6. 3 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) was developed by Binnig *et. al.* The principle of contact-mode AFM is schematically shown in **Fig. 2-18**. An AFM has a sharp tip attached to a micro-cantilever arm that is on the order of a few hundred micro-meters long. The cantilever is scanned along the sample surface, and it bends upward or downward with the surface atomic-scale unevenness by an atomic force. This shifts

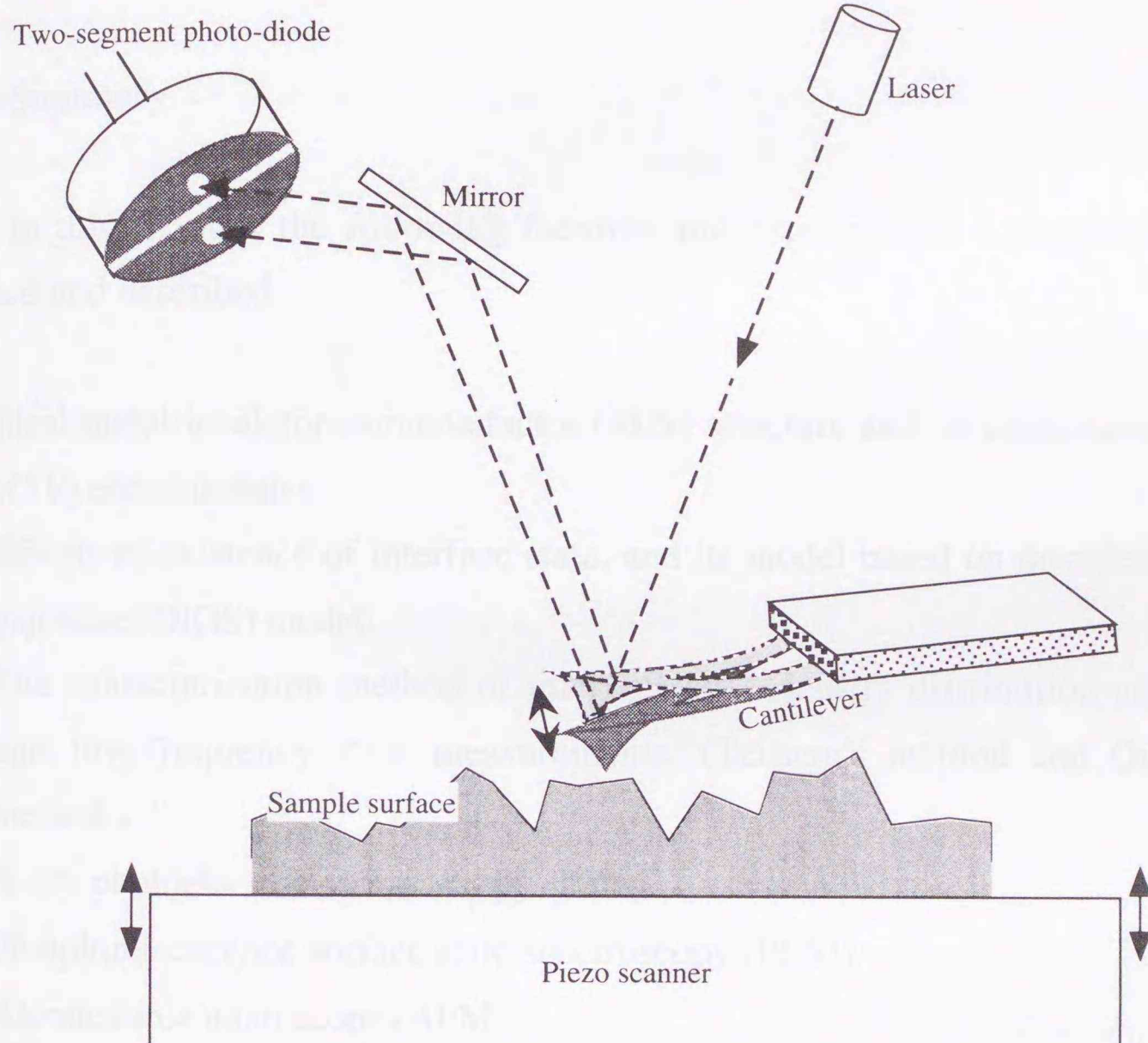


Fig. 2-18 Principle of AFM.

the beam between upper and lower photodiode components, creating voltage differences. These differences are used as feedback signals of applied voltages to the z-direction piezo-scanner, so as to keep the two-segment photodiode voltages the same. Thus, the topographic height information can be detected.

2.7 Summary

In this chapter, the following theories and experimental equipments are explained and described.

- (1) Ideal metal-insulator-semiconductor (MIS) structure and its capacitance-voltage (C - V) characteristics.
- (2) Effects of existence of interface state, and its model based on disorder-induced-gap-state (DIGS) model.
- (3) The characterization method of interface state density distribution using high- and low-frequency C - V measurements. (Terman's method and Quasi-static method.)
- (4) X-ray photoelectron spectroscopy (XPS).
- (5) Photoluminescence surface state spectroscopy (PLS³).
- (6) Atomic force microscope (AFM).

References

- 1) T. Yoshida, H. Hasegawa and T. Sakai: Jpn. J. Appl. Phys. **38** (1999) 2349.
- 2) T. Sakai, M. Kohno, S. Hirae, I. Nakatani and T. Kusuda: Jpn. J. Appl. Phys. **32** (1993) 4005.
- 3) T. Saitoh, H. Iwadate and H. Hasegawa: Jpn. J. Appl. Phys. **30** (1991) 3750.
- 4) T. Saitoh and H. Hasegawa: Appl. Surf. Sci. **56-58** (1992) 94.
- 5) T. Sawada, K. Numata, S. Tohdoh, T. Saitoh and H. Hasegawa: Jpn. J. Appl. Phys. **32** (1993) 511.
- 6) S. M. Sze: "PHYSICS OF SEMICONDUCTOR DEVICES" *Second-edition* (John Wiley & Sons, Inc., 1981) 362.
- 7) E. H. Nicollian and J. R. Brews, "MOS(Metal Oxide Semiconductor) Physics and Technology" (Wiley, New York, 1982) 319.
- 8) H. Hasegawa, H. Ohno: J. Vac. Sci. Technol. **B4** (1986) 1130.

Chapter 3 Ultrahigh-Vacuum Contactless Capacitance-Voltage Measurement Method

3.1 Introduction

To further advance the Si complementary metal-oxide-semiconductor (CMOS) technology to its ultimate scaling limits as well as to develop new nano-devices such as Si-based single electron transistors, it becomes increasingly important to understand and to control delicate changes of Si surface properties due to nano-structure processing. Since all the processing steps for semiconductor device fabrication are usually carried out on or through surfaces, electronically active near-surface defects introduced during processing can deteriorate the performance of nano-devices which are extremely sensitive to surfaces and interfaces.

In recent years, surface science type techniques such as scanning tunneling microscopy (STM),¹⁻³⁾ x-ray photoelectron spectroscopy (XPS),^{4,5)} etc have made great progress in characterization of microscopic structures and chemical compositions of surfaces. However, there has been no well-established non-destructive method for in-situ and quantitative characterization of the electronic properties of semiconductor surfaces before and after processing. One of the future candidates for such an *in-situ* electronic characterization may be the scanning capacitance microscopy (SCaM) technique recently reported by several groups.⁶⁻⁹⁾ In this technique, scanned capacitance measurement is carried out between nanometer-sized scanning tip and the sample surface, and a capacitance image of the surface is obtained. This technique can detect variations of local electronic properties with an extremely high spatial resolution. However, since the electric field distribution is highly nonuniform in atomic scale in the vicinity of the tip and its details are usually unknown, quantitative analysis of the measured capacitance to determine important parameters of the

sample such as doping density, band bending and surface state density, is extremely difficult and practically impossible at the present stage of development.

In this chapter, a novel ultrahigh-vacuum (UHV) contactless capacitance-voltage (C - V) method¹⁰⁾ is described, which we have recently developed to overcome the above difficulty, using a parallel-plate-type capacitance probe which provides a uniform electric field distribution. This system is expansion of the air-gap based C - V measurement system (CV-8000, Dainippon Screen Mfg. Co., Ltd., reported in 1993)¹¹⁾, which is also powerful for characterization of semiconductor surface properties¹²⁻¹⁴⁾. Although the spatial resolution of the present method is much poorer than that of the S Ca M technique, it allows a full quantitative analysis of the measured capacitance data. After the description of the measurement method and system, a theoretical calculation using the optical measurement of the UHV-gap length and its accuracy are described, demonstrating the capabilities of the system for non-destructive determination of conduction type, doping density, surface/interface state density distribution and Fermi level pinning position.

This UHV contactless C - V technique is also very powerful for characterization of UHV processing of compound semiconductor as discussed elsewhere.¹⁵⁻¹⁸⁾

3.2 Principle of C - V measurement in contactless fashion

The principle of contactless capacitance-voltage (C - V) measurement is simple and easy to understand for who know the conventional C - V method. As described in Sec. 2-2, the resistance of the insulator must be infinity. However, the thickness of insulator film becomes smaller than 3 nm, the direct tunneling current flows through the insulator layer even if the perfect insulating film could be formed (**Fig. 3-1 (a)**). To avoid this, as shown in **Fig. 3-1 (b)**, the field electrode for the capacitance measurement is placed above the sample surface separated by a narrow air- or UHV-gap (the UHV-gap is mainly used to realize a contactless C - V measurement, in this study), while the metal electrode is deposited and is adhered directly on the sample surface in a conventional C - V method. The capacitance measurements are carried out with

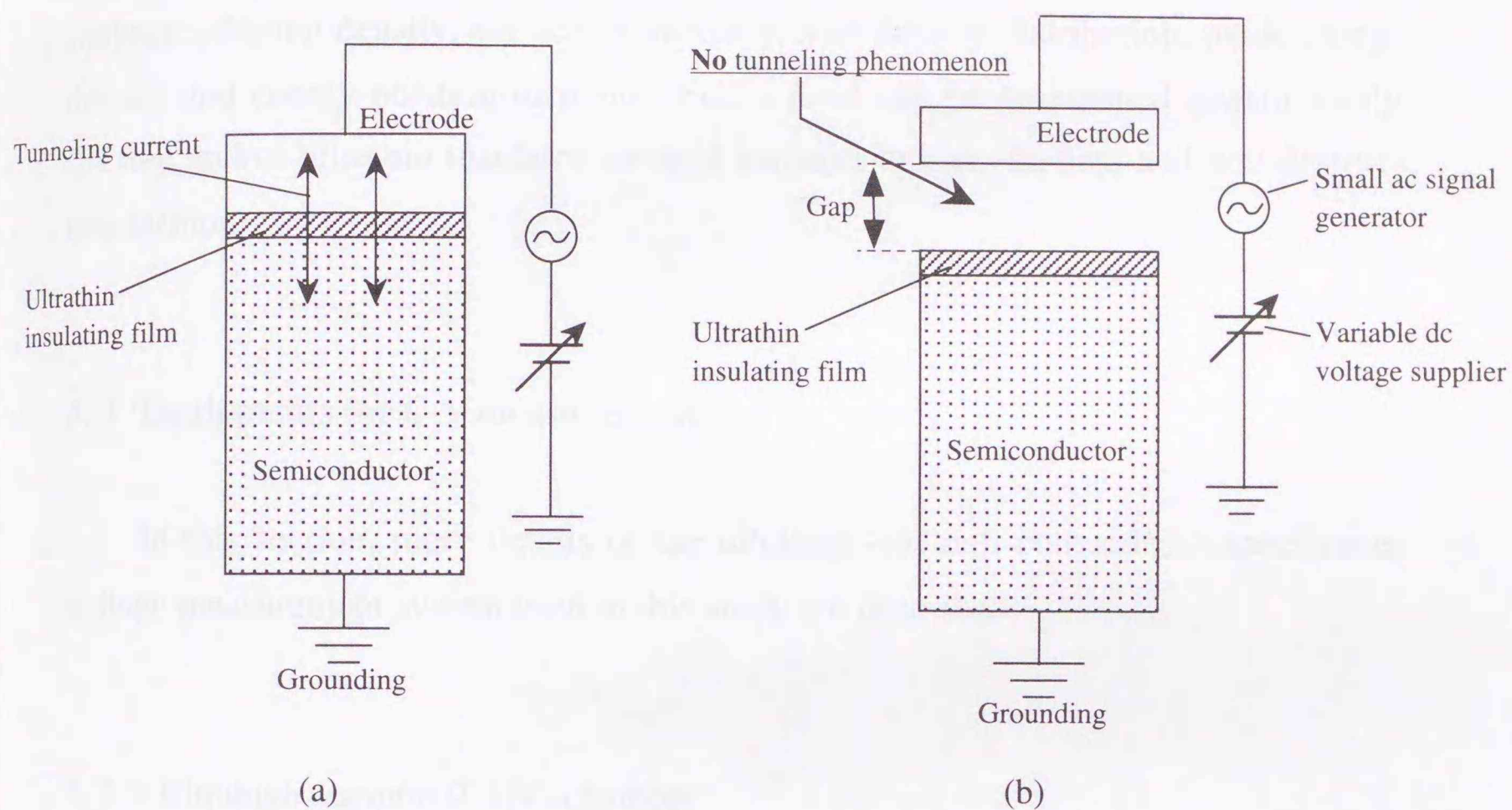


Fig. 3-1 (a) Conventional capacitance-voltage (C-V) measurement for ultrathin-insulator covered surface and (b) a principle of C-V measurement in contactless fashion.

changing the dc bias voltage on the field electrode. Considering this narrow gap as an additional "UHV-insulator", a conventional metal-insulator-semiconductor (MIS) assessment¹⁹⁾ of semiconductor free surfaces or ultrathin insulator-covered surfaces became possible. Thus, by using this contactless *C-V* measurement system, conduction type, doping density, surface or interface state density distribution, oxide charge density and energy position of pinned Fermi level can be determined quantitatively for free and/or ultrathin insulator covered surfaces in a contactless and non-destructive fashion.

3.3 Equipments for *C-V* measurement

In this section, more details of the ultrahigh-vacuum contactless capacitance-voltage measurement system used in this study are described.

3.3.1 Ultrahigh-vacuum (UHV) chamber

Figure 3-2 shows the schematic diagram of the ultrahigh-vacuum contactless capacitance-voltage measurement system. The samples were transferred from other chambers into the UHV *C-V* chamber using a special vertical transfer mechanism and a movable sample stage in UHV. With adjustments by the computer, the samples were placed exactly under the *C-V* sensor head. In this study, the sample was attached to a standard molybdenum sample holder generally used for molecular beam epitaxy (MBE) growth. A turbo molecular pump with a rotary pump connected in series was used to evacuate air from the chamber. And care was taken to make all the parts "bakable" to achieve the base pressure of 1×10^{-9} torr. In this system, since the variation of UHV-gap length caused by any kinds of vibrations leads the error of capacitance values, the system was carefully protected from vibrations. For this purpose, the *C-V* chamber was placed on an anti-vibration support stage with a weight of about three hundred kgs and a resonance frequency of several Hz. Buffer

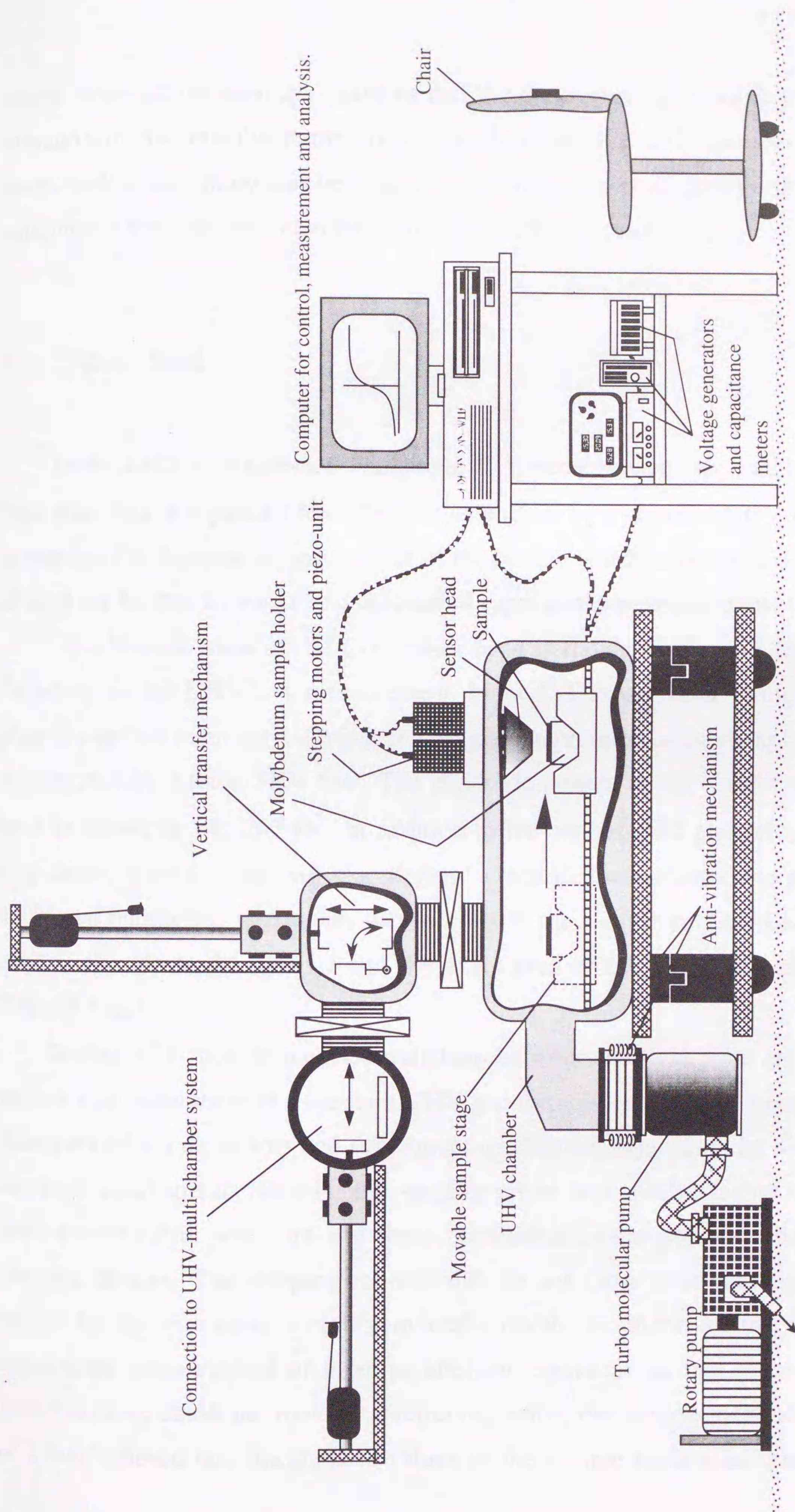


Fig. 3-2 Schematic diagram of ultrahigh-vacuum capacitance-voltage measurement system used in this study.

sheets were put between the chamber and the turbo molecular pump to prevent the vibration of the vacuum pumps from traveling into the *C-V* chamber. The system developed in this study can be attached to various types of growth and processing equipments for electronic characterization of each processing step.

3. 3. 2 Sensor head

In the UHV contactless *C-V* method, *C-V* measurements are carried out from a field plate that is separated from the sample surface by a constant UHV gap. The *C-V* sensor head is the most important part of the system which is connected to a computer used for feedback control and automated capacitance measurements.

A schematic view of the *C-V* sensor head is shown in **Fig. 3-3 (a)** along with the set-up for the UHV *C-V* measurement. In the *C-V* sensor head, a ring-shaped field plate is attached to an optical prism for the gap length measurement explained later. It is protected by a thick SiO_2 film. The electrode pattern at the bottom of the sensor head is shown in **Fig. 3-3 (b)**. In addition to the central field plate electrode with a ring shape, three surrounding "parallelism" electrodes were formed to provide three additional parallelism capacitors with respect to the sample surface. Chromium was used as the electrode material and the exact area of the field plate electrode was $7.49 \times 10^{-3} \text{ cm}^2$.

During *C-V* measurements, parallelism between the field plate and the sample surface was maintained at a constant UHV gap through capacitance measurements of three parallelism capacitors and subsequent mechanical adjustment by a piezoelectric feedback mechanism. Namely, the sensing probe was mechanically supported by three piezoelectric actuators and three mechanical screw actuators driven by the stepping motors. The stepping motors and the actuators were automatically controlled by the computer which provided suitable feedback on the basis of the capacitance measurement of three parallelism capacitors so that three capacitance values became equal and took an appropriate value. For achievement of planar gaps of a few hundred nm, the flatness values of the sample surface and the prism can

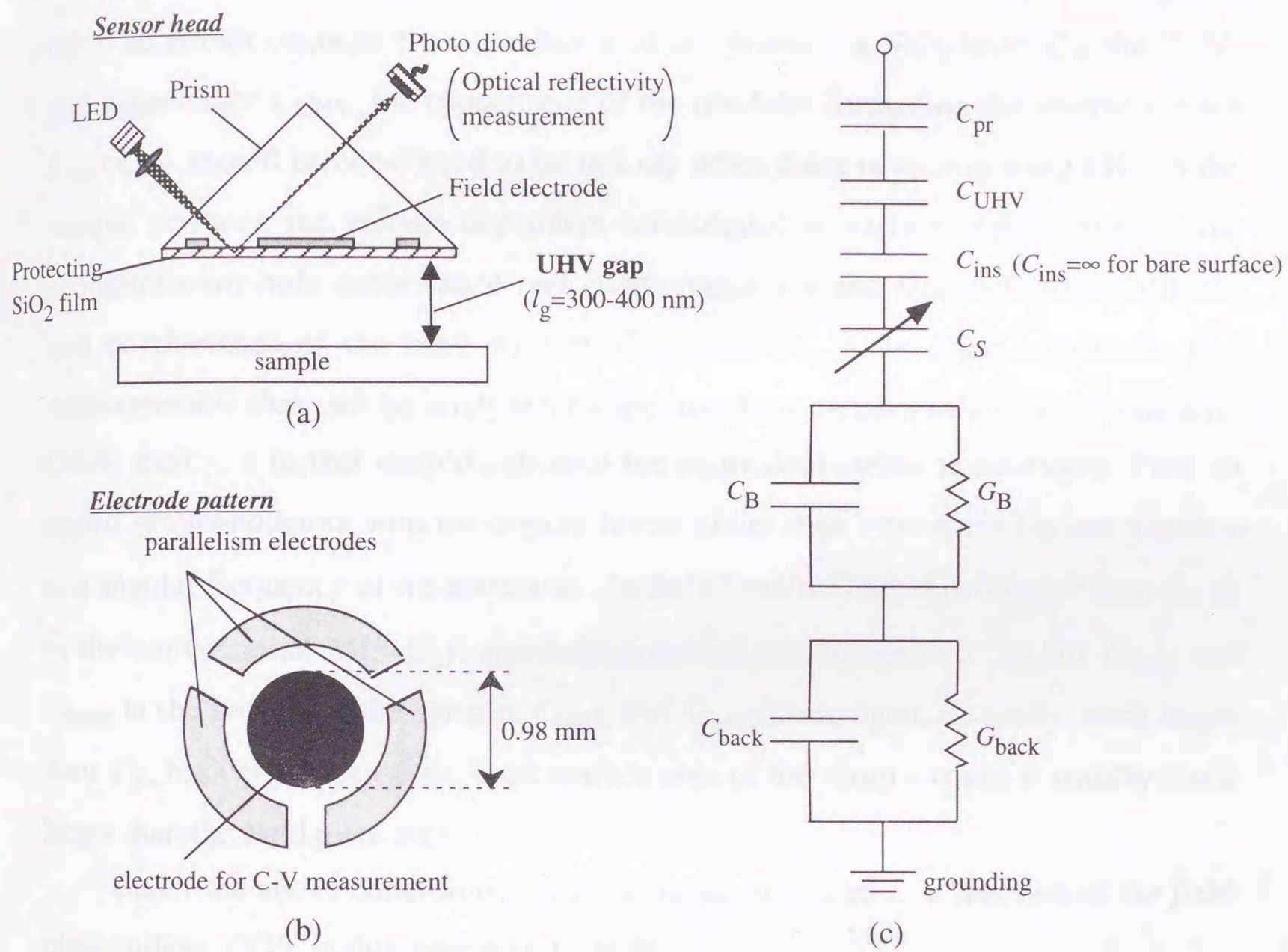


Fig. 3-3 Schematic view of (a) the C-V sensor head and (b) the electrode pattern. (c) Electrical equivalent circuit of the system.

become crucial. In this study, root mean square (RMS) flatness values of the wafer and the prism used here were typically 0.5-1.0 nm and 6-7 nm over the entire field plate area.

The electrical equivalent circuit of the measurement system is shown in **Fig. 3-3 (c)**. The circuit contains the capacitance of the protecting SiO₂ layer C_{pr} , the UHV-gap capacitance C_{UHV} , the capacitance of the insulator formed on the sample surface C_{ins} (C_{ins} should be considered to be infinity when there is no insulating film on the sample surface), the voltage dependent semiconductor surface capacitance C_S , the semiconductor bulk capacitance and conductance C_B and G_B , and the capacitance and conductance of the back contact, C_{back} and G_{back} . In order to perform C - V measurements that can be analyzed by the standard metal-insulator-semiconductor (MIS) theory, a further simplification of the equivalent circuit is necessary. First, in doped semiconductors with the doping levels rather than 10^{14} cm^{-3} , C_B and G_B/ω (ω is a angular frequency of measurement, $2\pi \cdot 5 \times 10^5 \text{ rad/sec}$) are much larger than C_S as in the conventional MIS C - V measurements and can be ignored. As for C_{back} and G_{back} at the bottom of the sample, C_{back} and G_{back}/ω are again normally much larger than C_S , basically because the back surface area of the sample wafer is usually much larger than the field plate area.

Under the above conditions, the capacitance measured as a function of the field plate voltage, $C(V)$, in this system is given by

$$\frac{1}{C(V)} = \frac{1}{C_{pr}} + \frac{1}{C_{ins}} + \frac{1}{C_{UHV}} + \frac{1}{C_S(V)} \bigg|_{\frac{1}{C_{ins}} = 0 \text{ for free surface}} \quad (3-1)$$

Thus, for analysis of the C - V data, the value of C_{UHV} or the length of the UHV-gap, l_g , should be known. Direct electrical measurement of C_{UHV} is, however, difficult, because it is always series connected to an unknown $C_S(V)$ which depends on various semiconductor parameters and voltages. Thus in this study, the UHV-gap length, l_g , was measured optically using the Goos-Hänchen effect in optics similar to the air-gap based C - V measurement system (CV-8000, Dainippon Screen Mfg. Co., Ltd.)¹⁰⁾. In this technique, the reflectivity of a totally reflecting prism, attached to the

C - V sensor head shown in **Fig. 3-3 (a)**, is measured. Here, the reflectivity becomes less than unity by the presence of the sample surface due to disturbance of the evanescent wave (Goos-Hänchen effect)²⁰. In the present system, a P-polarized laser beam was emitted onto the prism of the sensing probe and the reflected laser light (a semiconductor laser diode with a wavelength $\lambda=0.780 \mu\text{m}$) was detected by a photodiode.

3.3.3 Measurement of gap-length between sensor head and sample surface

To determine the UHV-gap length from the measured reflectivity, the reflectivity was calculated as a function of the UHV gap length, solving Maxwell's equations. In case of the simplest three-layer model shown in **Fig. 3-4 (a)**, the reflectivity R for the P-polarized light used in the present UHV contactless C - V system is calculated as

$$R = \left| \frac{r_0 + r_1 \exp(i\delta)}{1 + r_0 r_1 \exp(i\delta)} \right|^2 \quad (3-2)$$

where r_0 and r_1 are reflectivity coefficients of the upper and lower interfaces in **Fig. 3-4 (a)** and δ is the phase rotation angle; given respectively by

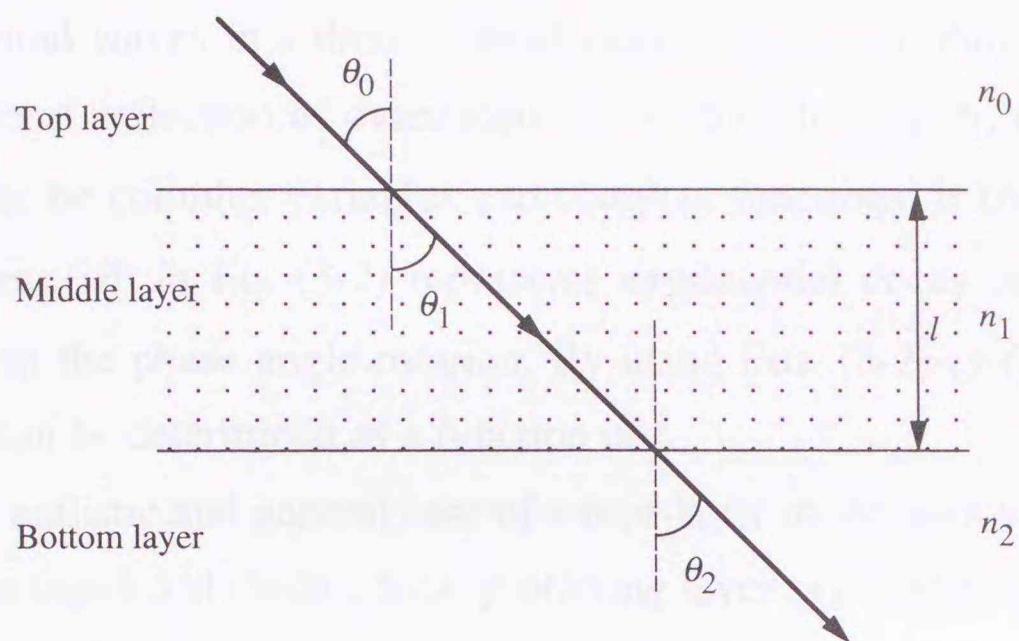
$$r_0 = \frac{n_1 \cos \theta_0 - n_0 \cos \theta_1}{n_1 \cos \theta_0 + n_0 \cos \theta_1}, \quad (3-3)$$

$$r_1 = \frac{n_2 \cos \theta_1 - n_1 \cos \theta_2}{n_2 \cos \theta_1 + n_1 \cos \theta_2}, \quad (3-4)$$

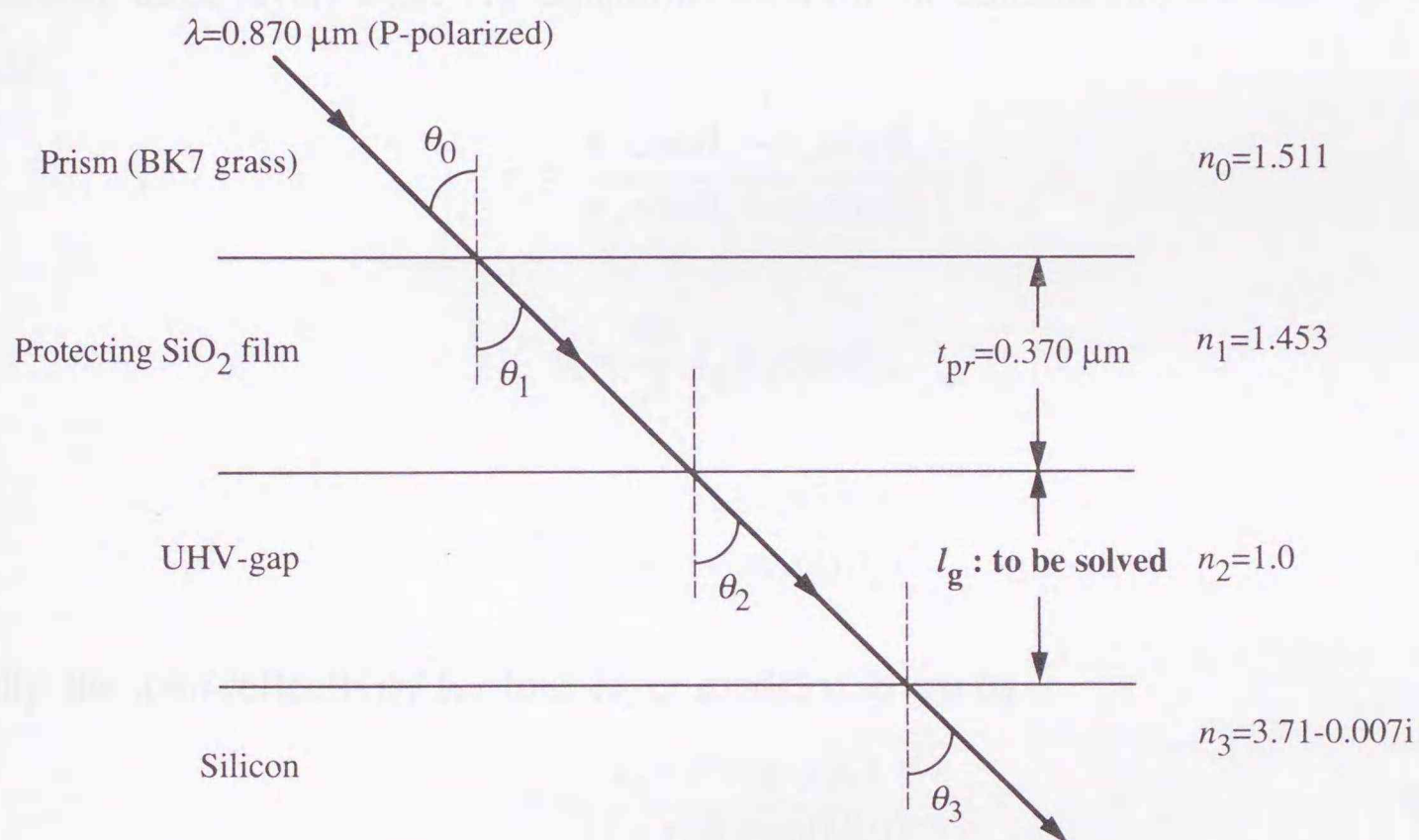
$$\delta = \frac{4\pi}{\lambda} l n_1 \cos \theta_1. \quad (3-5)$$

Here, n_0 , n_1 and n_2 are the refractive indices, θ_0 , θ_1 and θ_2 are the angles in **Fig. 3-4 (a)**, λ is the wavelength of laser, and l is the length of the middle layer. The angles θ_0 , θ_1 and θ_2 satisfy the following relationship according to Snell's law.

$$n_0 \sin \theta_0 = n_1 \sin \theta_1 = n_2 \sin \theta_2 \quad (3-6)$$



(a)



(b)

Fig. 3-4 Structures for the calculation of the reflectivity. (a) Standard three-layer model and (b) realistic four-layer model (bare Si).

The above equations are general ones applicable for normal reflection of non-evanescent normal waves in a three-layered system. However, they can be used for the present case of reflection of evanescent waves by allowing θ_1 , θ_2 , $\sin \theta_1$, $\sin \theta_2$, $\cos \theta_1$, $\cos \theta_2$ to be complex variables and complex functions. It should be noted in this case that $\exp(i\delta)$ in Eq. (3-2) represents exponential decay of the evanescent wave rather than the phase angle rotation. By using Eqs. (3-2)-(3-6) on computers, the value of R can be determined as a function of l .

In a more realistic and general case of a four-layer model shown in **Fig. 3-4 (b)**, where the prism ($n_0=1.511$) with a SiO_2 protecting layer ($n_1=1.453$, thickness $t_{\text{pr}}=370$ nm), UHV gap ($n_2=1.0$, gap-length l_g to be solved) and Si ($n_3=3.71-0.007i$), the total reflectivity can be calculated by repeated use of the above equations, starting from the bottom three layers first. The equations used for the calculations are Eqs. (3-3), (3-4) and

$$r_2 = \frac{n_3 \cos \theta_2 - n_2 \cos \theta_3}{n_3 \cos \theta_2 + n_2 \cos \theta_3}, \quad (3-7)$$

$$\delta_2 = \frac{4\pi}{\lambda} l_g n_2 \cos \theta_2, \quad (3-8)$$

$$R' = \frac{r_1 + r_2 \exp(i\delta_2)}{1 + r_1 r_2 \exp(i\delta_2)}, \quad (3-9)$$

finally, the total reflectivity for four-layer model is given by

$$R = \left| \frac{r_0 + R' \exp(i\delta_1)}{1 + r_0 R' \exp(i\delta_1)} \right|^2 \quad (3-10)$$

here, the δ_1 is same as in Eq. (3-5). Additionally, the sample has a surface layer such as an oxide layer, the calculation of total reflectivity has to be carried using five-layer model. The equations to be used for the calculation are given by Eqs. (3-3), (3-4), (3-7), (3-8) and

$$r_3 = \frac{n_4 \cos \theta_3 - n_{\text{sl}} \cos \theta_4}{n_4 \cos \theta_3 + n_{\text{sl}} \cos \theta_4}, \quad (3-11)$$

$$\delta_3 = \frac{4\pi}{\lambda} t_{sl} n_{sl} \cos \theta_3, \quad (3-12)$$

$$R' = \frac{r_2 + r_3 \exp(i\delta_3)}{1 + r_2 r_3 \exp(i\delta_3)}, \quad (3-13)$$

$$R'' = \frac{r_1 + R' \exp(i\delta_3)}{1 + r_1 R' \exp(i\delta_3)}, \quad (3-14)$$

where t_{sl} and n_{sl} are the thickness and refractive index of surface layer, respectively. Then, the total reflectivity for five-layer model is given by

$$R = \left| \frac{r_0 + R'' \exp(i\delta_1)}{1 + r_0 R'' \exp(i\delta_1)} \right|^2, \quad (3-15)$$

here, the δ_1 is same as in Eq. (3-5).

The examples of the calculated reflectivity for the laser incident angle of $\theta_0=45^\circ$, wavelength of $\lambda=780$ nm, and the SiO_2 protecting film thickness of $t_{pr}=370$ nm is shown in **Fig. 3-5** as a function of the UHV gap length for the free and oxide covered Si surfaces. The refractive indices used here were 1.511, 1.453, 1.0 and 3.71-0.007i for prism glass (BK7 glass), SiO_2 , UHV gap and Si, respectively. The thicknesses and refractive indices of oxide layers covering the silicon surfaces are 50 nm and 100 nm and 1.453, respectively. The reflectivity shows large variation for $l_g=100$ -600 nm, thus accurate measurements of the UHV gap length should be possible in this range.

Here, one of unique features of the contactless C-V method is the application to the bare semiconductor surfaces mentioned before. However, the bare semiconductor surface, in practical cases, has an unknown ultrathin surface layers such as natural oxide layer, adsorbed layer or surface reconstructed layer with unknown values of t_{sl} and n_{sl} . Then, the optical reflectivity modification caused by such a layer results in errors in the UHV-gap length determination. In order to provide ideas in the magnitudes of error caused by presence of such an unknown layer, calculated results are shown in **Fig. 3-6** for the cases that fairly thick layer with $t_{sl}=5$ nm thickness and refractive index values of $n_{sl}=1.0$ and 4.0 are present on Si surface. The result for bare Si surface with no surface layer is also shown as a reference. These three curves

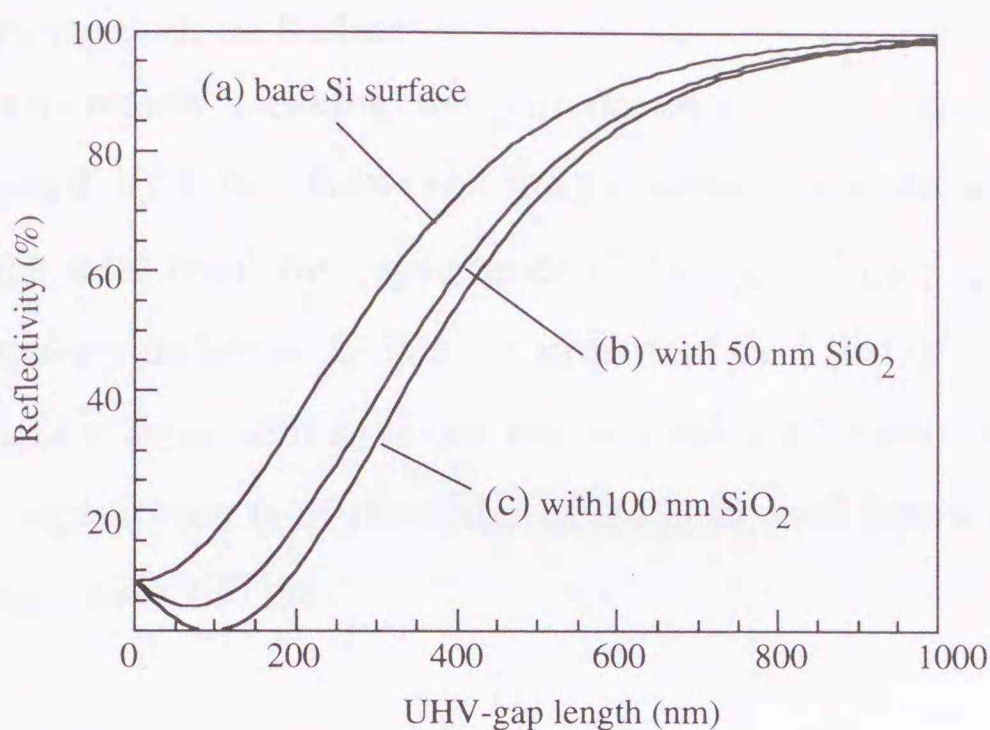


Fig. 3-5 Calculated reflectivity as a function of the UHV-gap length for (a) bare Si surface and (b),(c) Si surfaces covered with 50 nm and 100 nm SiO_2 films, respectively. A line (a) was obtained using 4-layer model and (b),(c) were obtained using 5-layer model.

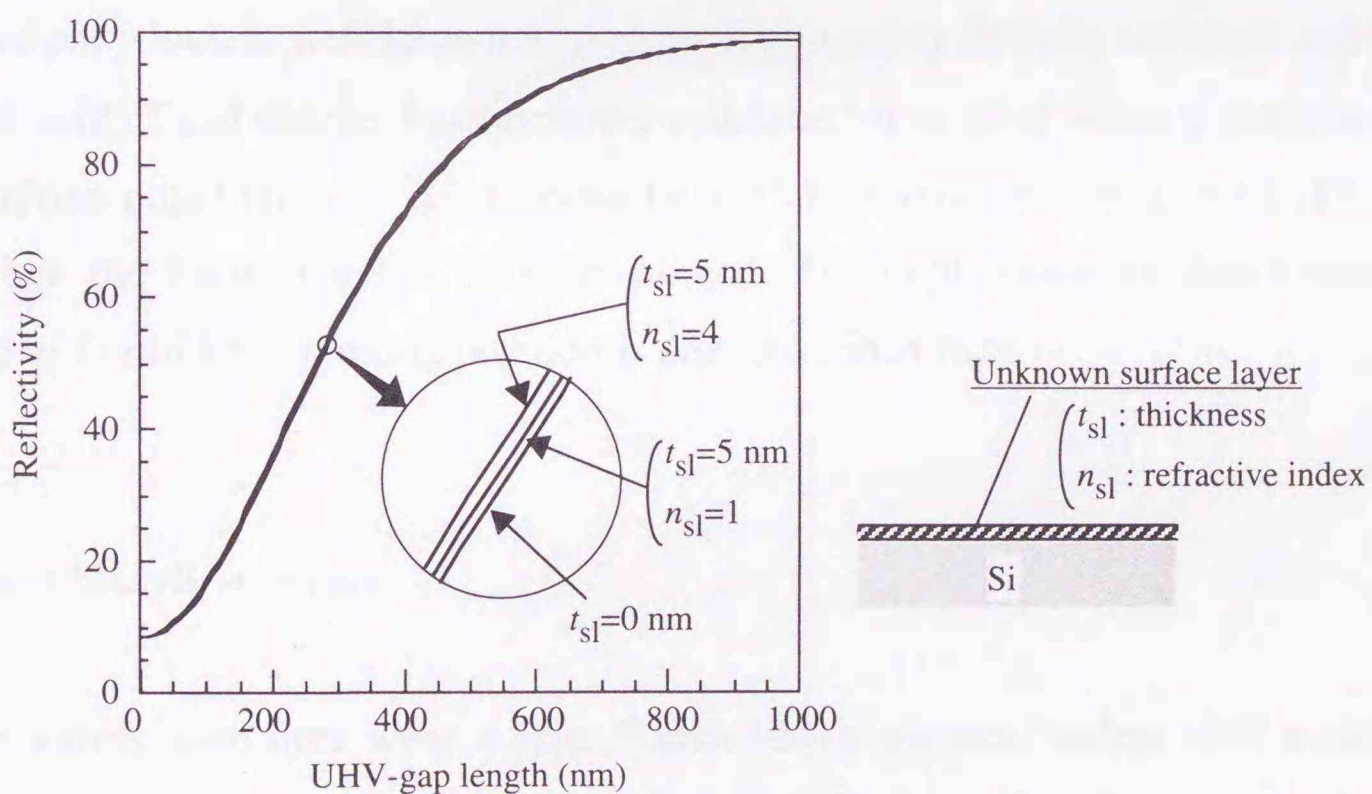


Fig. 3-6 Calculated reflectivity as a function of the UHV-gap length for Si surfaces with unknown surface layer.

almost overlap with each other.

Approximately speaking, the presence of a surface layer leads to overestimating the gap length by t_{sl}/n_{sl} . However, the presence of the surface layer also effectively reduces the total insulator capacitance $C_I (= C_{pr}^{-1} + C_{UHV}^{-1})$. It should be noted that accurate determination of C_I is more important than that of the gap length here. For a typical surface layer with $t_{sl}=1$ nm and any value of refractive index, the error in the insulator capacitance is of the order of 0.1% or well below 0.1% for measurements with l_g larger than 100 nm.

3.4 Example of ultrahigh-vacuum contactless capacitance-voltage measurement

In order to investigate the capabilities of the novel system, UHV contactless C - V measurements were carried out on high-temperature thick thermal oxide covered silicon surface which is well known to possess high quality SiO_2/Si interface and low density of oxide fixed charge. Furthermore, a surface Fermi level pinning position can be determined quantitatively using contactless C - V method changing the UHV-gap length when the Fermi level is strongly pinned. The explanation of determination technique of Fermi level pinning position is also described here.

3.4.1 Thick SiO_2/Si interface

The wafers used here were n-type 5 inch (001)-oriented wafers with a carrier concentrations of $4\text{-}5 \times 10^{14} \text{ cm}^{-3}$ and $2\text{-}3 \times 10^{15} \text{ cm}^{-3}$. To form Si surfaces covered with a high-temperature thick thermal oxide, the Si surfaces were oxidized in dry oxygen at a substrate temperature of 1000°C for 1 hour and annealed in a nitrogen atmosphere at the same temperature for 1 hour. This resulted in the formation of 100-nm-thick thermal oxide on Si surfaces.

Figure 3-7 shows an example of the UHV contactless C - V curve obtained from

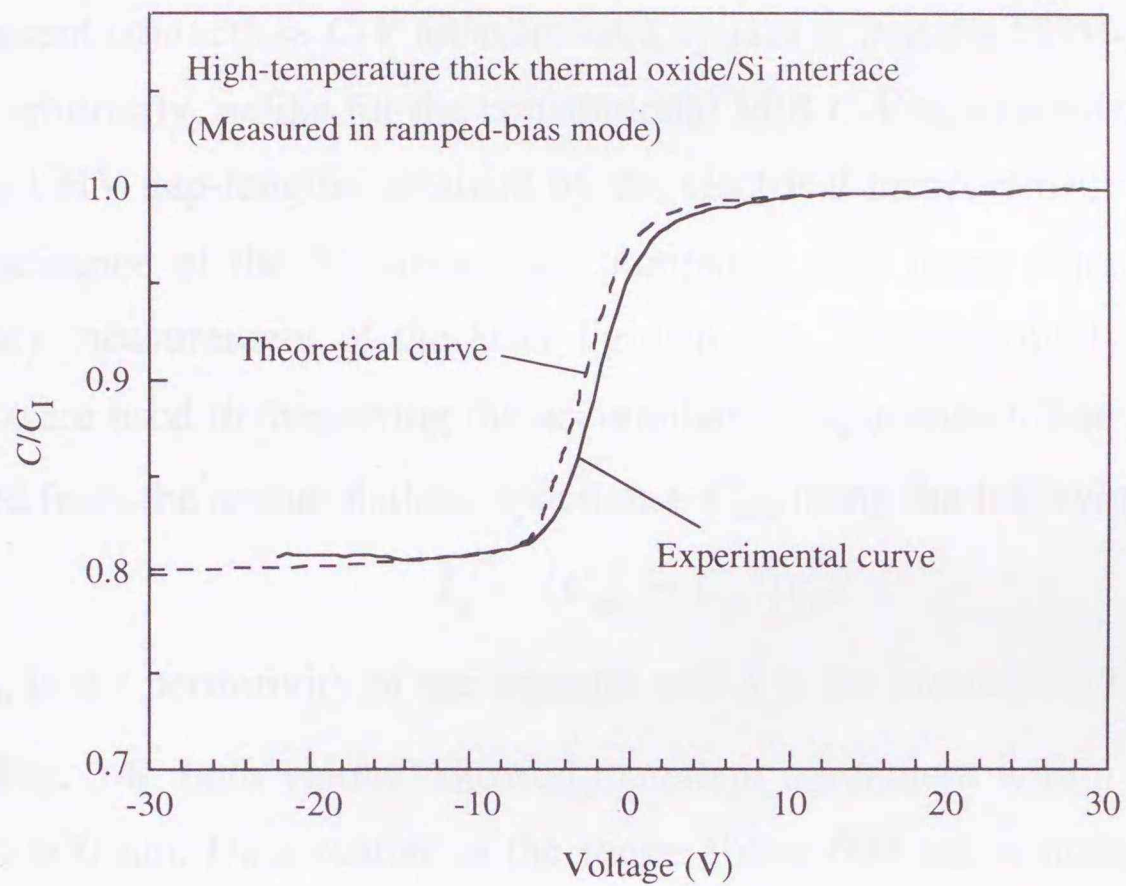


Fig. 3-7 Typical UHV contactless C - V curve of the Si(001) surface with high-temperature thick thermal oxide.

Si surface covered with a high-temperature thick thermal oxide measured in ramped bias mode. The C - V curve was found to be in excellent agreement with the calculated ideal curve, indicating that the interface state density was extremely low.

Since $C_s(V)$ in Eq.(3-1) becomes infinitely large under the accumulation bias (positive bias) condition, the capacitance measurement under this condition provides a different method of measuring the UHV-gap length. Furthermore, a unique feature of the present contactless C - V measurement system is that the UHV-gap length can be changed arbitrarily, unlike for the conventional MIS C - V measurements.

The UHV gap-lengths obtained by the electrical measurement of the accumulation capacitance of the Si surface are compared with those determined by optical reflectivity measurement of the laser light in **Fig. 3-8**. Thermally oxidized silicon surfaces were used in measuring the accumulation capacitance. The gap-length l_g was calculated from the accumulation capacitance C_{acc} using the following formula,

$$l_g = (C_{acc}^{-1} - C_{pr}^{-1}) \epsilon_0 S \quad (3-16)$$

where ϵ_0 is the permittivity of the vacuum and S is the area of the field electrode. As seen in **Fig. 3-8**, both values showed excellent agreement within the range of 200 nm up to 600 nm. Data scatter in the range above 600 nm is mainly caused by the error of the optical measurements at larger gap-lengths caused by exponential decay of the evanescent wave. Thus, it can be concluded that the optical measurement gives reliable values of the gap-length below 600 nm. The fact that the line has a slope of unity and passes through the origin confirms that the surface is free from Fermi level pinning in this case. This, in turn, means that the surface Fermi-level position can be determined for the "free" surfaces with Fermi level pinning.

The present system allows the determination of the conduction type and doping concentration. To determine these, pulsed bias was used to obtain deep depletion C - V behavior, where the gate voltage was supplied by such a pulse wave form that the generation rate of minority carrier could not follow the sweep rate of the pulsed mode bias. **Figure 3-9** shows examples of such $1/C^2$ - V plots for different doping levels and different UHV-gap lengths. The negative slopes of these plots show that these materials are n-type. The calculated carrier concentration values from the lower three

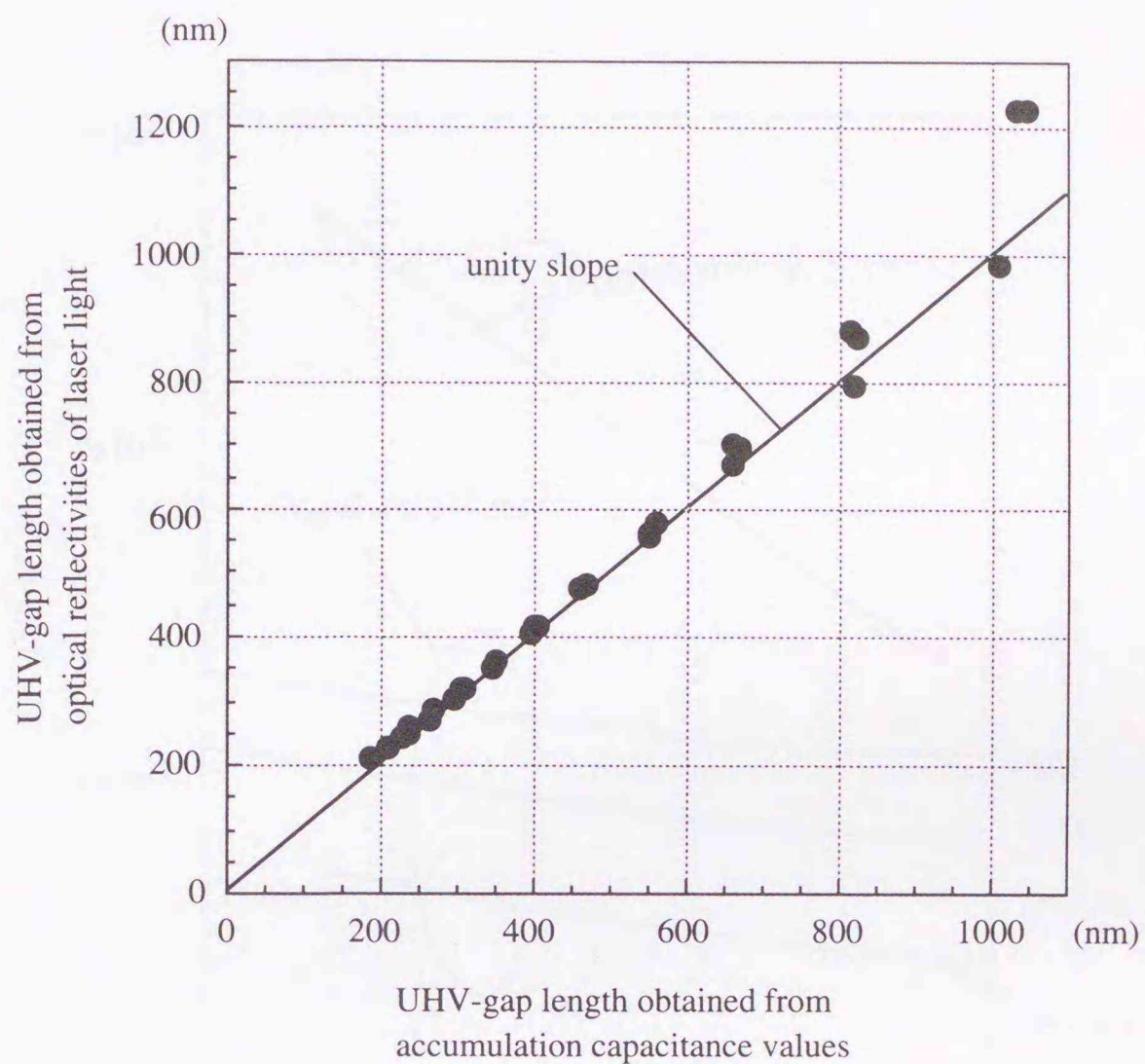


Fig. 3-8 Comparison between the UHV-gap length obtained from optical reflectivity measurements of laser light and that determined by the electrical measurement of the accumulation capacitance of the Si surface covered with high-temperature thick thermal oxide.

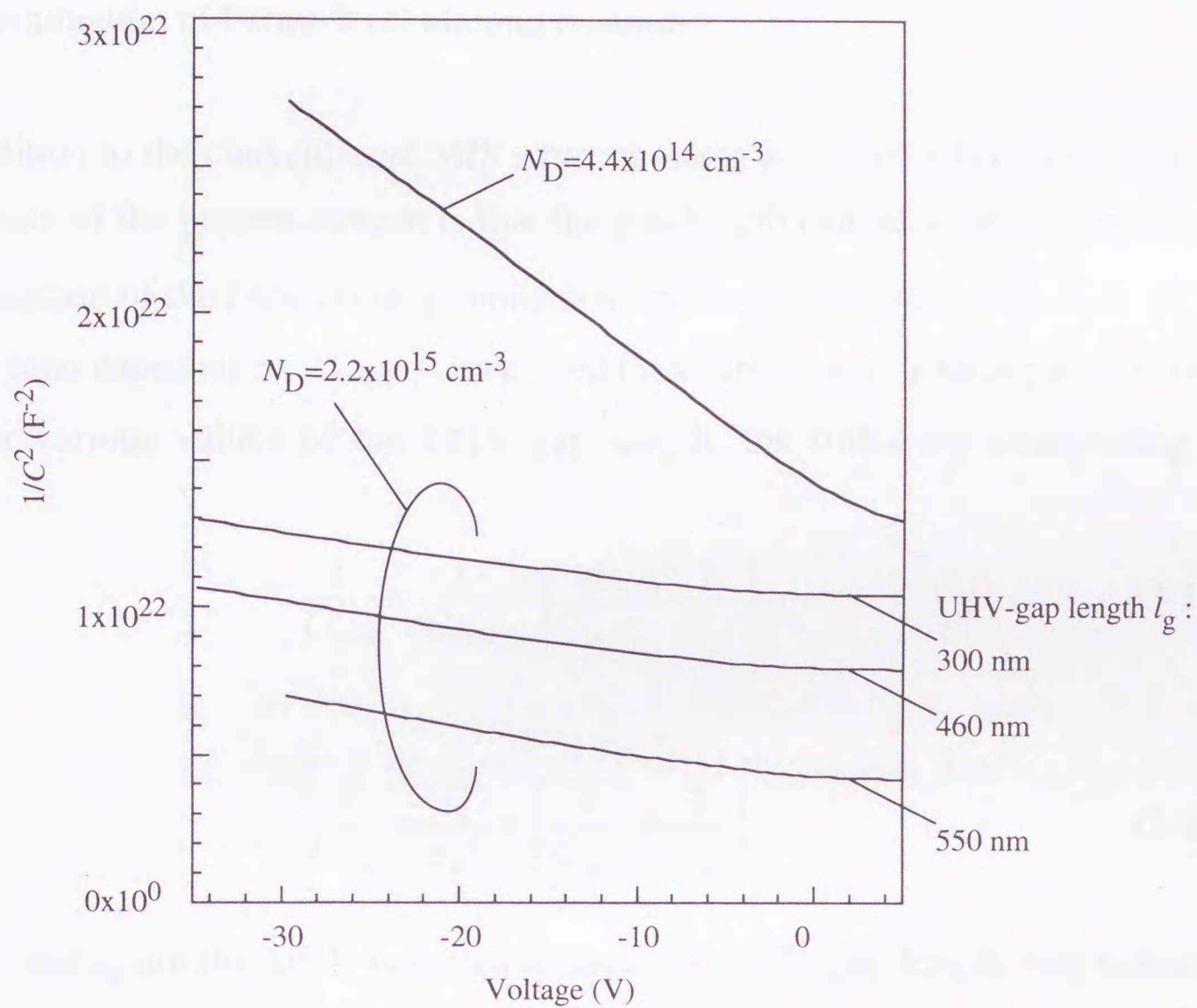


Fig. 3-9 The $1/C^2$ -V plots with various lengths of UHV-gap and different carrier concentration values.

plots showing parallel shifts with the UHV-gap length change as expected, is $4.4 \times 10^{14} \text{ cm}^{-3}$, and that from the upper plot is $2.2 \times 10^{15} \text{ cm}^{-3}$. These values are in excellent agreement with the Hall effect measurements.

3.4.2 Determination of Fermi-level pinning position

In addition to the conventional MIS measurements at a fixed UHV gap length, a unique feature of the present system is that the gap length can be varied. This allows the determination of the Fermi level pinning position in the following way.

If the total capacitance, C_{total} , is measured on a surface with a strong Fermi level pinning for various values of the UHV gap length, the following relationship is observed,

$$\frac{1}{C_{\text{total}}} = \frac{1}{C_{\text{UHV}}} + \left(\frac{1}{C_{\text{spin}}} + \frac{1}{C_{\text{pr}}} \right), \quad (3-17)$$

or

$$\frac{1}{C_{\text{total}}} = \frac{l_g}{\epsilon_0 S} + \left(\frac{1}{C_{\text{spin}}} + \frac{1}{C_{\text{pr}}} \right). \quad (3-18)$$

Here C_{UHV} and l_g are the UHV-gap capacitance and UHV-gap length, respectively, obtained from the optical gap-length measurement, C_{pr} is the known capacitance value of the protecting SiO_2 film for the sensor head surface and C_{spin} is the constant semiconductor depletion layer capacitance corresponding to the band bending caused by Fermi level pinning. From the intercept value of the C_{total}^{-1} versus C_{UHV}^{-1} plot or C_{total}^{-1} versus l_g plot, which should be equal to $\left(C_{\text{pr}}^{-1} + C_{\text{spin}}^{-1} \right)$, the surface Fermi level pinning position can be determined.

Here, it should be mentioned that variations of C_{spin} with UHV-gap length variation due to contact potential difference are ignored, since the field electrode is separated about 100-500 nm from the sample surface. With such a large gap, typical work-function difference values between Cr field plate of 0.5-1.0 eV cannot affect

the surface potential appreciably even in the most sensitive case of non-existence of surface Fermi level pinning.

3.5 UHV-based multi-chamber system

Generally, it is well known that many kinds of semiconductor surfaces before and after processing steps react with air actively; mainly the surfaces are oxidized and contaminated by oxygen, water, organic matter, particles, and so on in the air. These phenomena change the surface conditions, which cause the miss-understanding on the development and optimization of device processing. Therefore, the surfaces after processing such as MBE-growth, plasma exposure, ultrathin-film formation, dry etching, ... should be transferred keeping UHV environment until various kinds of characterization and further processing steps.

In this study, the complete UHV contactless *C-V* system was connected to a UHV-based multi-chamber system equipped in the super-clean room of the Research Center for Interface Quantum Electronics, Hokkaido University, as shown in **Fig. 3-10**. The 17 UHV-chambers including chambers for XPS measurement, PL measurement, contactless *C-V* measurement, electron-cyclotron-resonance (ECR)-plasma processing, high-temperature UHV annealing, etc are connected via UHV transfer tunnel or UHV-suitcase. Back pressures of an UHV tunnel and an UHV suitcase are always kept to the order of 10^{-10} Torr using combination of ion-sputtering pumps and titanium-sublimation pumps, and every processing and analysis chambers are kept to suitable pressures using suitable pump-systems each other.

The sample can be introduced into this UHV system through a load-lock system which is pumped out from atmospheric pressure into the order of 10^{-8} Torr using series connection of rotary pump and turbo molecular pump.

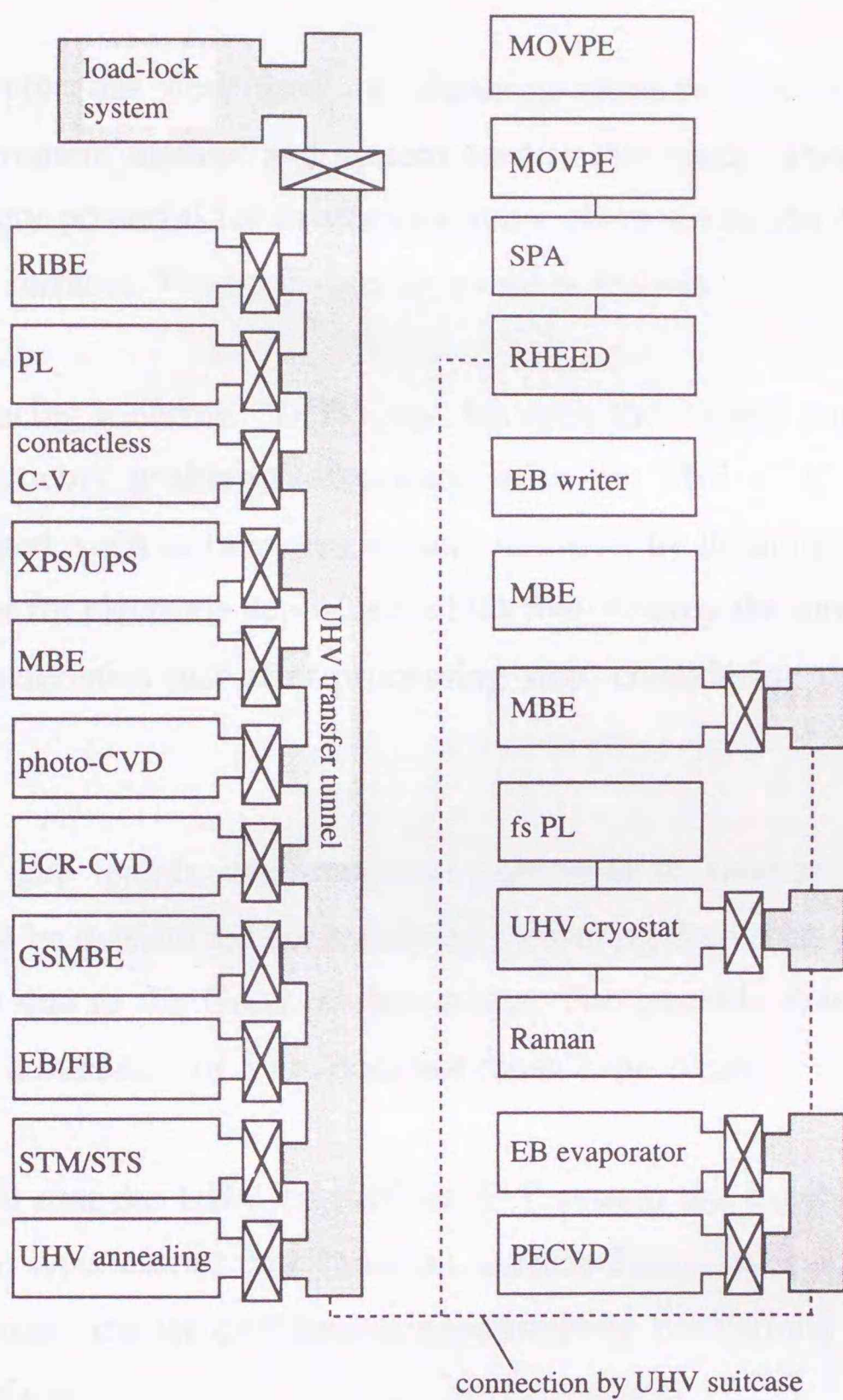


Fig. 3-10 UHV-based growth/fabrication/characterization system used in this study.

3.6 Summary

This chapter has described an ultrahigh-vacuum contactless capacitance-voltage measurement method and system used in this study. This method has been shown to be very powerful for *in-situ* electronic characterization of various kinds of semiconductor surfaces. The main summaries are as follows.

- (1) By introducing a narrow "UHV-gap" between the sample surface and the field electrode, many problems associated with the MIS C - V technique can be circumvented, such as tunneling current transport by thinning down of insulating layer, labor for electrode deposition which may destroy the intrinsic surface/interface characteristics just after processing step, considering the leakage current, and so on.
- (2) The UHV-gap length, one important parameter to analyze the measured C - V curves, can be determined accurately by measuring the variation of reflectance of laser light due to the Goos-Hächen effect. The possible existence of a surface layer with a thickness of 5 nm does not cause large errors.
- (3) It is shown that the UHV contactless C - V system has capabilities to determine conduction type, carrier concentration, surface Fermi level position and surface/interface state density distribution quantitatively for various kinds of semiconductor surfaces.
- (4) This UHV contactless C - V measurement system is connected to UHV-based multi-chamber-system, which leads *in-situ* characterization after various kinds of processing steps such as plasma treatment, chemical vapor deposition (CVD), molecular beam epitaxy (MBE) growth, UHV annealing, ... without exposing into the air.

References

- 1) Y. Morita and H. Tokumoto: Appl. Phys. Lett. **67** (1995) 2654.
- 2) D. Huang and Y. Yamamoto: Jpn. J. Appl. Phys. **35** (1996) 3734.
- 3) M. Niwa, T. Kouzaki, K. Okada, M. Udagawa and R. Sinclair: Jpn. J. Appl. Phys. **33** (1994) 388.
- 4) T. Aiba, K. Yamauchi, Y. Shimizu, N. Tate, M. Katayama and T. Hattori: Jpn. J. Appl. Phys. **34** (1995) 707.
- 5) H. Ogawa and T. Hattori: Appl. Phys. Lett. **61** (1992) 577.
- 6) C. C. Williams, W. P. Hough and S. A. Rishton: Appl. Phys. Lett. **55** (1989) 203.
- 7) C. C. Williams, J. Slinkman, W. P. Hough and H. K. Wickramasinghe: Appl. Phys. Lett. **55** (1989) 1662.
- 8) H. Tomiye, H. Kawami, M. Izawa, M. Yoshimura and T. Yao: Jpn. J. Appl. Phys. **34** (1995) 3376.
- 9) H. Tomiye, T. Yao, H. Kawami and T. Hayashi: Appl. Phys. Lett. **69** (1996) 4050.
- 10) T. Yoshida, H. Hasegawa and T. Sakai: Jpn. J. Appl. Phys. **38** (1999) 2349.
- 11) T. Sakai, M. Kohno, S. Hirae, I. Nakatani and T. Kusuda: Jpn. J. Appl. Phys. **32** (1993) 4005.
- 12) T. Sakai, M. Kohno, H. Okada, H. Matsubara and S. Hirae: Jpn. J. Appl. Phys. **36** (1997) 935.
- 13) M. Kohno, S. Hirae, H. Okada, H. Matsubara, I. Nakatani, Y. Imaoka, T. Kusuda and T. Sakai: Jpn. J. Appl. Phys. **35** (1996) 5539.
- 14) T. Sakai, M. Kohno, S. Hirae, I. Nakatani, H. Matsubara and T. Kusuda: Jpn. J. Appl. Phys. **35** (1996) 3311.
- 15) H. Takahashi and H. Hasegawa: Appl. Surf. Sci. **166** (2000) 526.
- 16) M. Mutoh, N. Tsurumi and H. Hasegawa: Jpn. J. Appl. Phys. **38** (1999) 2538.
- 17) H. Takahashi, T. Yoshida, M. Mutoh, T. Sakai and H. Hasegawa: Solid-State Elect. **48-8** (1999) 1561.
- 18) T. Hashizume, Y. Ishikawa, T. Yoshida and H. Hasegawa: Jpn. J. Appl. Phys. **37** (1998) 1626.

Chapter 4 Properties of Hydrogen-Terminated Silicon Surfaces

4.1 Introduction

Recently, a deal of notice have been taken on surface cleaning technique in silicon (Si) ultralarge-scale integrations (ULSIs). Hydrogen terminated Si surface is one of clean and stable surfaces and have been used as an initial surface for various kinds of advanced processes in the Si technology. Among these advanced processes, some of the processes such as molecular beam epitaxial (MBE) growth of Si and SiGe, ultrathin insulator formation and atomic lithography require ultrahigh-vacuum (UHV) environments. As the device feature sizes are continuously reduced, necessity of UHV processing is expected to increase. Thus, understanding and control of the hydrogen-terminated surface in UHV environments will become increasingly important. More specifically, it is desirable to realize a UHV compatible well passivated surface with low surface state density and good thermal stability.

A deal of results for surface structure in atomic-scale and chemical and optical properties have been reported, for a long time, using surface science type techniques such as scanning tunneling microscopy (STM)^{1,2}, X-ray photoelectron spectroscopy (XPS)³⁻⁵ and infrared (IR) absorption spectroscopy⁶. Furthermore, scanning capacitance microscopy (SCaM)⁷⁻¹⁰, Kelvin-probe method^{11,12} and total-photoelectron-yield spectroscopy¹³⁻¹⁶, for example, are developed to determine the electronic properties of semiconductor surfaces. However, no-well established method for characterizing electronic properties is available yet for in-situ and quantitative characterization of hydrogen terminated Si surfaces.

In this chapter, an UHV contactless capacitance-voltage (C - V) technique^{17,18} was mainly applied for the characterization of electronic properties of surface. Using

this technique, the conventional metal-insulator semiconductor (MIS) assessment can be applied to pre- and post-processing semiconductor surfaces (details are described in chapter 3). So the quantitative and non-destructive characterization of electronic properties such as conduction type, carrier doping level, surface/interface state density distribution and surface Fermi level pinning position can be made for various kinds of hydrogen terminated Si surfaces. Furthermore, XPS, atomic force microscopy (AFM) and photoluminescence surface state spectroscopy (PLS³) are also applied to hydrogen terminated surfaces for the characterizations of the chemical/optical properties and for the observation of the surface structures in atomic-scale.

4.2 Preparation of sample surface

The wafers used in this study were n-type silicon with a carrier concentration of $2.5 \times 10^{15} \text{ cm}^{-3}$ for (111) surfaces and $4.4 \times 10^{14} \text{ cm}^{-3}$ for (100) surfaces. Here, conditions for hydrogen termination of (111)- and (100)-oriented Si surfaces are described.

4.2.1 (111)-oriented Si surfaces

For H-termination of Si surfaces, three types of treatment methods were used. One was so-called "*Higashi's method*"¹⁹). It consists of the removal of a conventional high temperature thick thermal oxide by buffered hydrofluoric acid solution (BHF), formation of native oxide in an HCl : H₂O₂ solution at 80°C for 10 min, followed by dipping in NH₄F (40%) solution at room temperature. This treatment is hereafter referred to as the BHF/H₂O₂/NH₄F treatment.

Other two types of treatment method were to use an NH₄F solution and to use an HF solution. The details were as follows. For the NH₄F treatment, the air-exposed bare Si wafer covered with a thin natural oxide was directly immersed into an NH₄F (40%) solution for 20-30 minutes. In this process, H₂ gas bubbles were generated by

the chemical reaction at the Si surface and disturbed the etching and flattening the Si surface. To avoid adsorption of such bubbles on the Si surface completely, the wafer was pulled up to the air for several times. This NH_4F treatment was applied also to p-type (111)-oriented surface. For the HF treatment, the bare Si wafer was immersed into an HF (0.5%) solution for 10 minutes. NH_4F and HF treatments were carried out at room temperature.

These three treatment methods include rinsing the wafers in deionized water for a couple of minutes. Finally, the wafers were completely dried by exposing into the dry N_2 gas flow.

Here, the "conventional high temperature thick thermal oxide" is formed by following way (this is same as Sec. 3.4.1). The Si surfaces were oxidized in dry oxygen at a substrate temperature of 1000°C for 1 hour and annealed in a nitrogen atmosphere at the same temperature for 1 hour. This resulted in the formation of 100-nm-thick thermal oxide films on Si surfaces with excellent interface properties.

4.2.2 (100)-oriented Si surfaces

For H-termination of Si (100) surfaces, the method proposed by Morita and Tokumoto²⁰⁾ was used. Here, a conventional high temperature thick thermal oxide is formed again as the first step, and then the wafer is dipped in $\text{HF} : \text{HCl} = 1 : 19$ solution for 2-3 min. In the actual process, the sample was dipped into the solution from one end to another with a constant and moderate speed. The removal of the oxide layer needs to proceed moderately toward [110] direction. Then, the surface was dried by dry N_2 gas without rinsing by water. This treatment is hereafter referred to as the HF/HCl treatment.

Both hydrogen terminated (111) and (100) surfaces were mounted onto 1 inch Mo-holder generally used for molecular-beam-epitaxy (MBE)-growth, and were introduced into the UHV-based multi-chamber system through a load-lock system immediately.

4.3 Properties of hydrogen-terminated Si surfaces

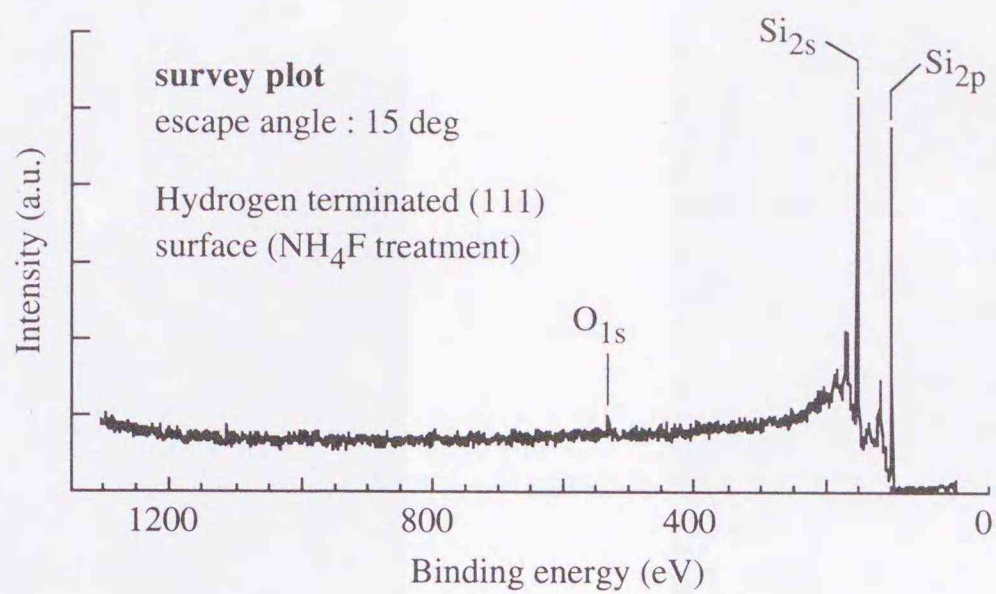
4.3.1 Chemical analysis by XPS measurement

Figure 4-1 shows the XPS spectra obtained from hydrogen terminated Si (111) surface prepared by NH_4F treatment. The escape angle of excited photoelectron was 15 degree. From the survey plot (**Fig. 4-1 (a)**), no component was detected except for silicon and traces of oxygen. To obtain more detail information, the narrow scan for Si2p region was applied (**Fig. 4-1 (b)**). A spin separation between $2p_{3/2}$ and $2p_{1/2}$ is clearly seen; the ratio of integral intensity of 0.5 and the difference of energy position of 0.6 eV²¹⁾. The shape of spectra are warped by existence of Si-H and Si-H₂ component which magnitude of chemical shift is 0.3-0.5 eV from Si-Si bonding state²²⁻²⁴⁾. And there was no oxide component originated from oxidized Si atoms, therefore, the oxygen component which was seen in survey scan plot was originated from adsorbed water or O₂ molecules, not from the silicon oxide.

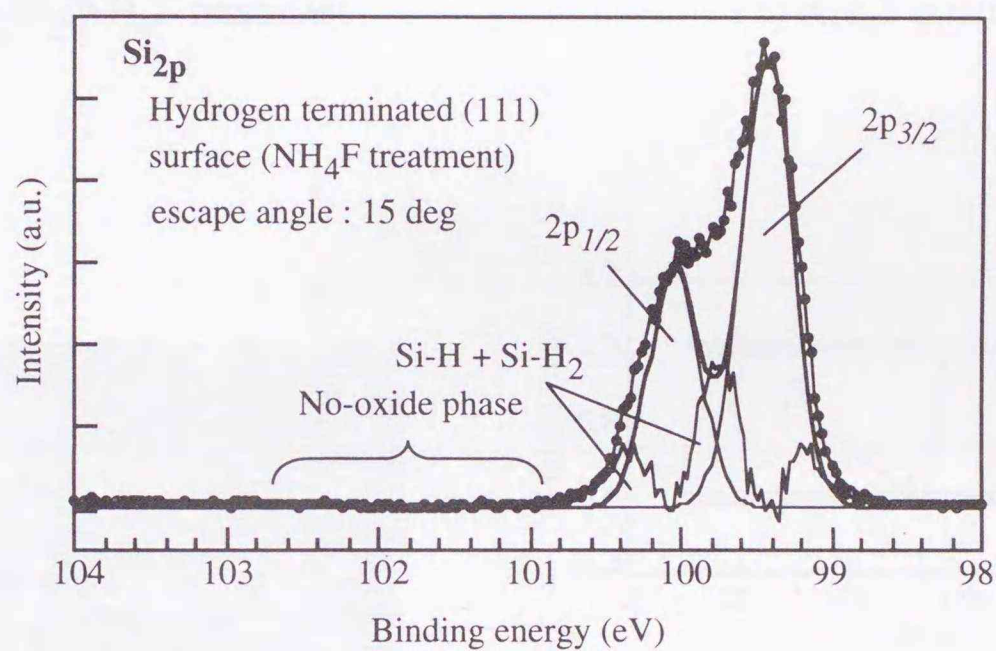
The accuracy of analysis using XPS is generally 0.1% at the very outside, which can not be considered as enough sensitive value for recent surface analysis. Anyway, it can be said that, at least from XPS analysis, hydrogen terminated surfaces used in this study were clean and oxide-free surfaces.

4.3.2 Nano-scale observation by AFM

Atomic force microscopy (AFM) was used for atomic scale observation of hydrogen terminated Si surfaces prepared by various treatment conditions. **Figure 4-2 (a)-(c)** show AFM images of hydrogen terminated Si surfaces prepared by BHF/H₂O₂/NH₄F treatment, NH₄F treatment and HF treatment, respectively. Wound and uneven striped patterns can be seen at the surfaces obtained from BHF/H₂O₂/NH₄F and NH₄F treatments. From the typical line profile shown in **Fig. 4-2 (d)**, the height of



(a)



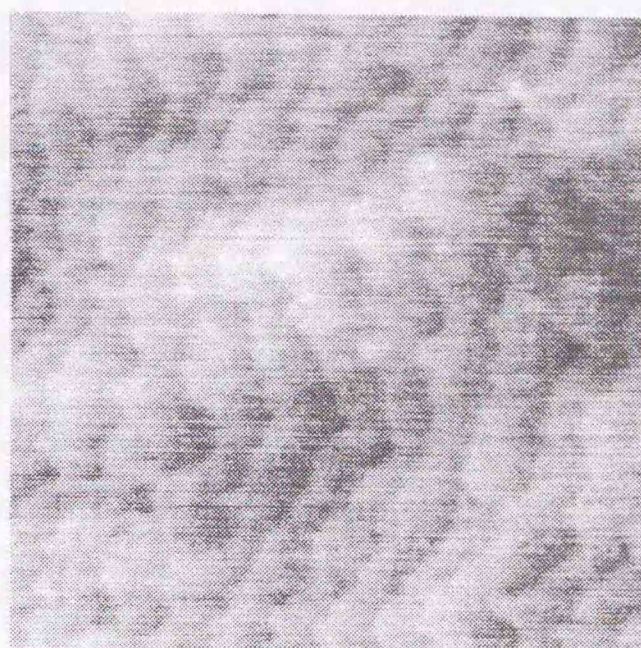
(b)

Fig. 4-1 XPS results of hydrogen terminated Si (111) surface prepared by NH_4F treatment.



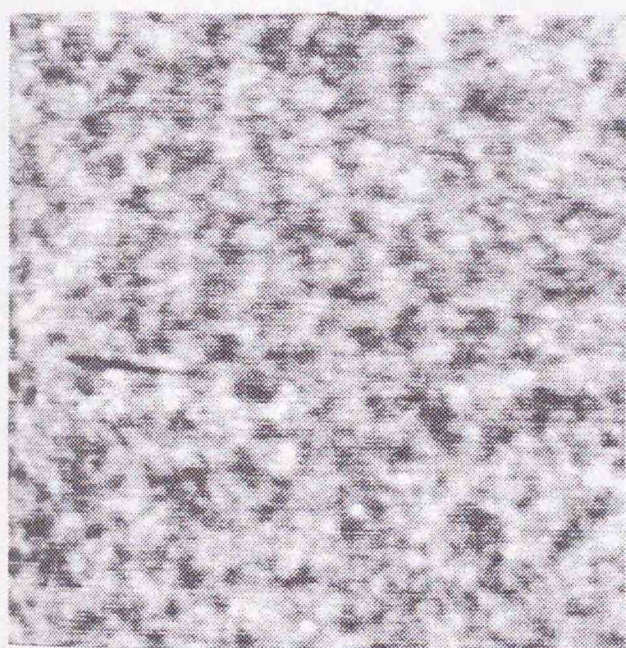
100 nm

(a) BHF/H₂O₂/NH₄F treatment



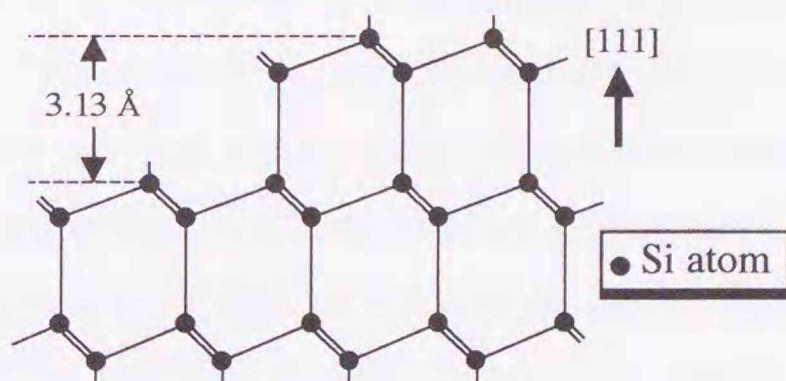
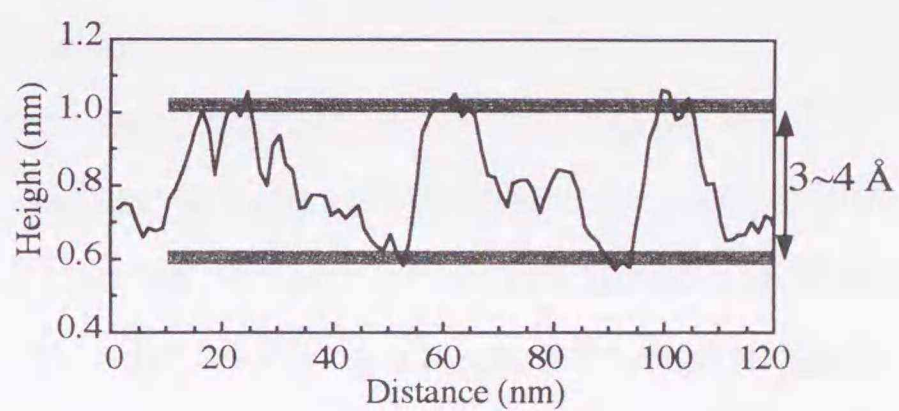
100 nm

(b) NH₄F treatment (10 min)



100 nm

(c) HF treatment



(d)

Fig. 4-2 (a)-(c) AFM images for hydrogen terminated Si(111) surfaces prepared by various kinds of treatment. (d) A typical line-profile of (b) and an illustration of atomic-step structure for (111)-oriented Si surface.

this striped patterns was about 3~4 Å. And the distance between (111) surfaces of Si can be calculated to 3.13 Å using the geometrical calculation of diamond structure (lattice constant : 5.43 Å). Thus, these striped patterns were considered to the terrace-step structure, which means these surfaces were extremely flat in atomic scale.

The ideal hydrogen terminated (111) surface possesses only Si-mono-hydride (Si-H) phase. However, the real (111) surface has an inclination (0.3-0.5 degree, in this study) which causes a terrace-step structure at the topmost layer. As shown in **Fig. 4-2 (d)**, the Si-di-hydride (Si-H₂) phase appears at the step-edge part, and these phase was detected in XPS Si2p spectrum shown in **Fig. 4-1 (b)**.

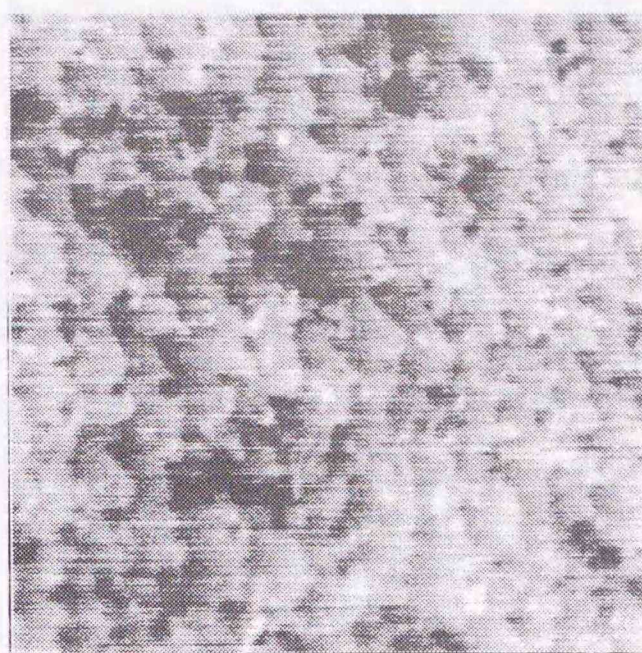
On the other hand, HF treated (111) surface did not show terrace-step structure (**Fig. 4-2 (c)**). It can be seen that the surface was covered with atomically uneven structure. It is known that the NH₄F solution creates the HF ions and excess OH ions by hydrolysis reaction, and the OH ion cut the Si-Si bonding and etches the Si surface. However, in HF solution, the ratio of etching Si is enough slow to be ignored. So the uneven structure in atomic scale remained.

Here, the shape of the surface terrace-step structure varies showing the relationship to the light intensity in treatment. **Figure 4-3 (a) and (b)** show the comparison of AFM images obtained from NH₄F treated surfaces, one was treated in light intensity of 0.1 mW which is supplied by a fluorescent lamp generally used in draft-chamber, and the other was in that of 3.0 mW supplied by a tungsten (W) bulb generally used to form strong white light. By exposing the sample surface to light with high intensity while the treatment, the surface became disordered structure keeping the terrace-step pattern. As mentioned before, the ideal hydrogen terminated (111) surface is described as the surface covered only with mono-hydride phase. So, the existence of step structure itself disturbs the realization of ideal condition, which means the length of step edge should be short anyway. (The shape of step edge flow should be linear rather than being wound.) Here, the surface treated in light intensity of 0.1 mW is better than the surface treated in that of 3.0 mW.

For more improvement of the step edge flow shape, the treatment time in NH₄F solution was examined. **Figure 4-4** shows the AFM image after 20 minuets treatment in NH₄F solution. It can be seen the improvement of the linearity of step edge flow.



(a) Light intensity : 0.1 mW



(b) Light intensity : 3 mW

Fig. 4-3 AFM images of hydrogen terminated Si (111) surfaces prepared by NH_4F treatments with white color light exposure; (a) 0.1 mW and (b) 3 mW, respectively.

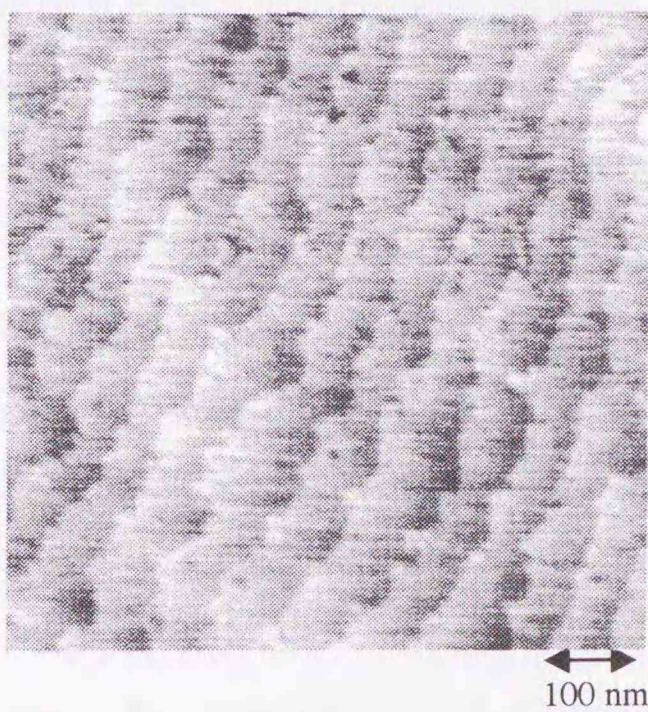


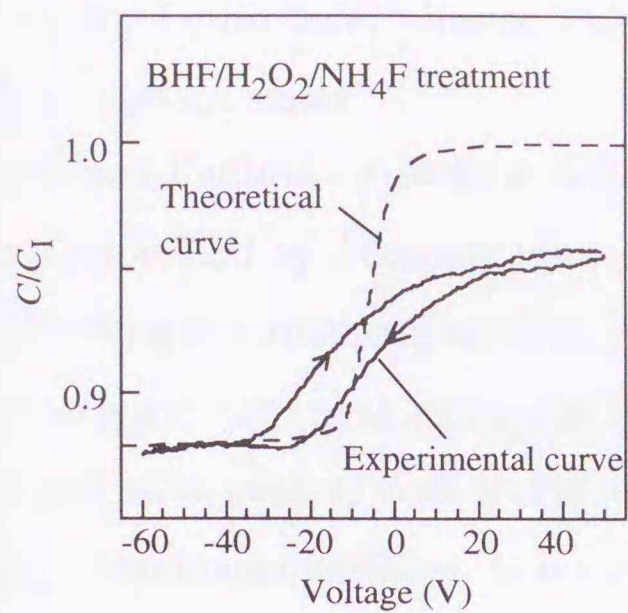
Fig. 4-4 AFM image of hydrogen terminated Si (111) surfaces prepared by NH_4F treatments. Treatment time was 20 min.

As mentioned above, the Si surface is etched by OH ions existing in the NH_4F solution. Here, the each topmost Si atoms of (111) surface (terrace region) is bonded to three Si atoms of second layer, while the each topmost Si atoms of (100) surface (step edge part) is bonded to only two Si atoms²⁵). So, it needs to cut three Si-Si bonds to remove one Si atom at (111) surface, while it needs to cut only two to remove one at (100) surface. Thus, the (111) surface is most stable for NH_4F solution, and the surface becomes atomically flat and is covered stable (111) surface. Such an anisotropic process leads selective etching of the protruding step edge. The treatment time in NH_4F solution has an effect on the distribution of surface state density characterized using contactless capacitance-voltage method^{26,27}). The details are written in Sec. 4-4.

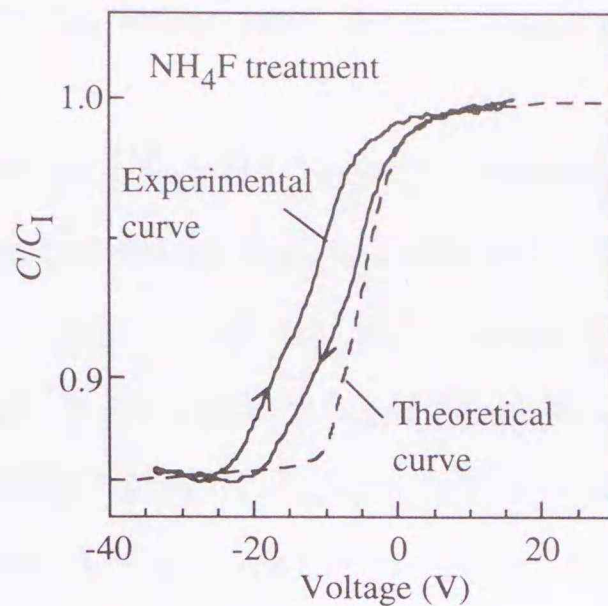
4. 3. 3 Electronic properties measured by UHV contactless C - V system

Figures 4-5 (a)-(c) show the UHV contactless C - V curves obtained from hydrogen terminated Si (111) surfaces treated with $\text{BHF}/\text{H}_2\text{O}_2/\text{NH}_4\text{F}$ treatment, HF treatment and NH_4F treatment, respectively. The broken lines indicate the ideal C - V curves calculated with the theory based on conventional MIS C - V assessment which has been described in Sec. 2-2. The series connection of capacitances of protecting SiO_2 film and UHV-gap was used as an insulator capacitance for the calculation of ideal curves. The UHV-gap capacitance was calculated using UHV-gap length determined optically. All capacitance values were normalized by the insulator capacitance value (= series connection of protecting SiO_2 and UHV-gap capacitances).

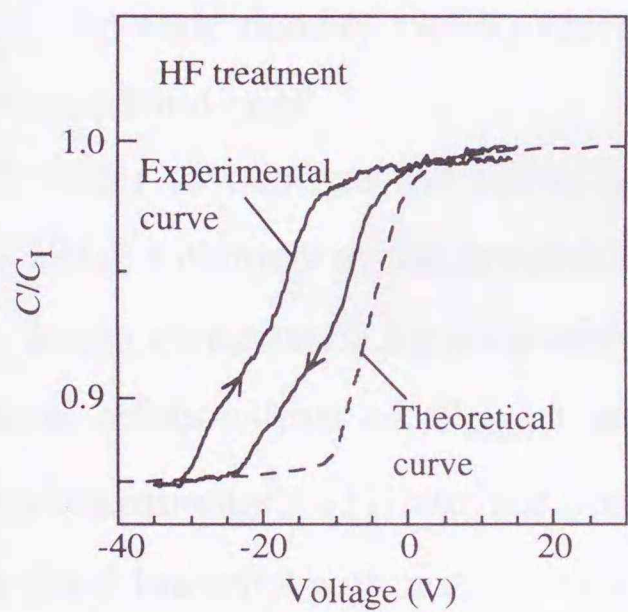
All of the C - V curves of hydrogen terminated (111) surfaces showed large hysteresis. This hysteresis has a clock-wise loop, thus it is an injection-type rather than the ion drift-type. The range of capacitance variation was normal for **(b)** NH_4F treated and **(c)** HF treated surfaces, showing the change from accumulation down to strong inversion. On the other hand, it was severely limited for $\text{BHF}/\text{H}_2\text{O}_2/\text{NH}_4\text{F}$



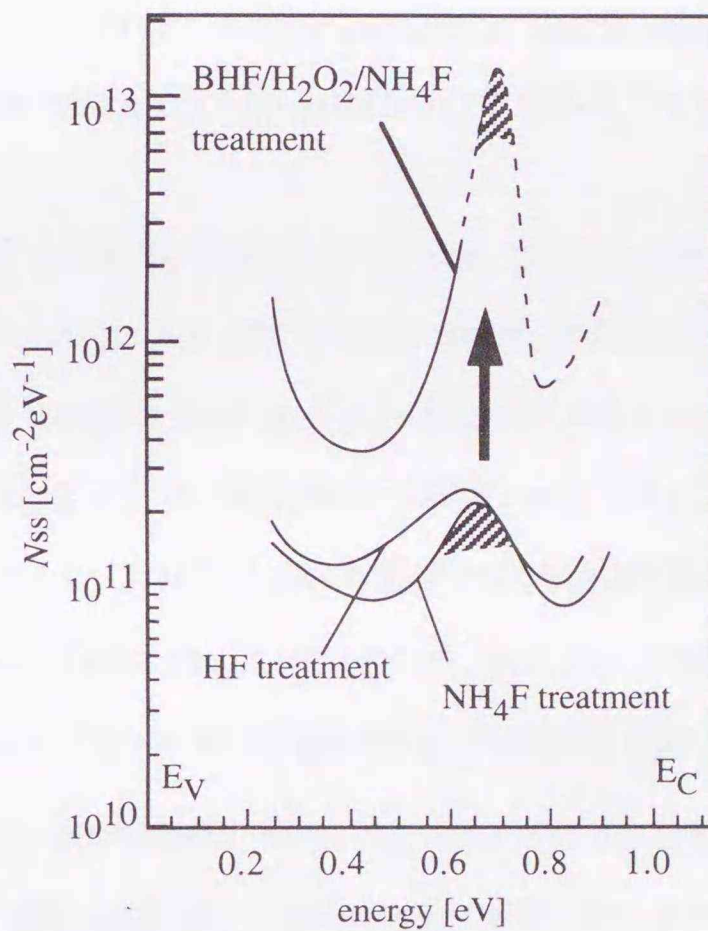
(a)



(b)



(c)



(d)

Fig. 4-5 UHV contactless C-V results for hydrogen terminated (111) surfaces prepared by (a) BHF/H₂O₂/NH₄F treatment, (b) NH₄F treatment and (c) HF treatment. The surface state density (N_{ss}) distributions calculated by Terman's method are also shown (d).

treated surface under the positive bias range towards accumulation. This indicates that a strong Fermi level pinning exists in the latter case, being caused by a large number of surface states.

The distributions of surface state density (N_{ss}) for hydrogen terminated (111) surfaces calculated by Terman's method are shown in **Fig. 4-5 (d)**. From this figure, both of hydrogen terminated surfaces prepared by NH_4F and HF treatments possess a discrete surface state peak at around 0.65eV from valence band edge. The height of the discrete state peak as well as the minimum value of N_{ss} are similar for these two hydrogen terminated surfaces. However, the discrete state peak of the surface after HF treatment is broader than that after NH_4F treatment. In the case of the surface prepared by BHF/ H_2O_2 / NH_4F treatment, the surface state density shown in **Fig. 4-5 (d)** also has a U-shaped distribution, but the width of distribution is much narrower. Namely, the state density rapidly increases at an energy position of 0.6-0.7 eV from the valence band edge.

In order to confirm the Fermi level pinning position of the surface by BHF/ H_2O_2 / NH_4F treatment at the positive bias range, the previously mentioned technique of measuring capacitance for different gap lengths was applied. **Figure 4-6** shows the measured relationships of C_{total}^{-1} and C_{UHV}^{-1} at different UHV-gap lengths for hydrogen terminated (111) surface prepared by BHF/ H_2O_2 / NH_4F treatment. The plot shows good linearity with a slope of unity. Then the intercept of this plot should be equal to $(C_{pr}^{-1} + C_{spin}^{-1})$. From this, the surface Fermi level pinning position was determined to be $E_F - E_V = 0.64$ eV. This result is consistent with the distribution shape of surface state density shown in **Fig. 4-5 (d)** and also consistent with the previous determination of the pinning position from XPS band-bending measurement. Thus, it seems to suggest that the pinning center in this surface is similar to the discrete defect of the other surfaces shown here, but its density is too high to go beyond the peak under the bias voltage used here, as shown in broken line of **Fig. 4-5 (d)**.

Then, the measured pulsed C-V curves of hydrogen terminated Si (111) surfaces prepared by NH_4F treatment and BHF/ H_2O_2 / NH_4F treatment are shown in **Figs. 4-7(a)** and **(b)**, respectively. Deep depletion behavior was clearly observed in the C-V

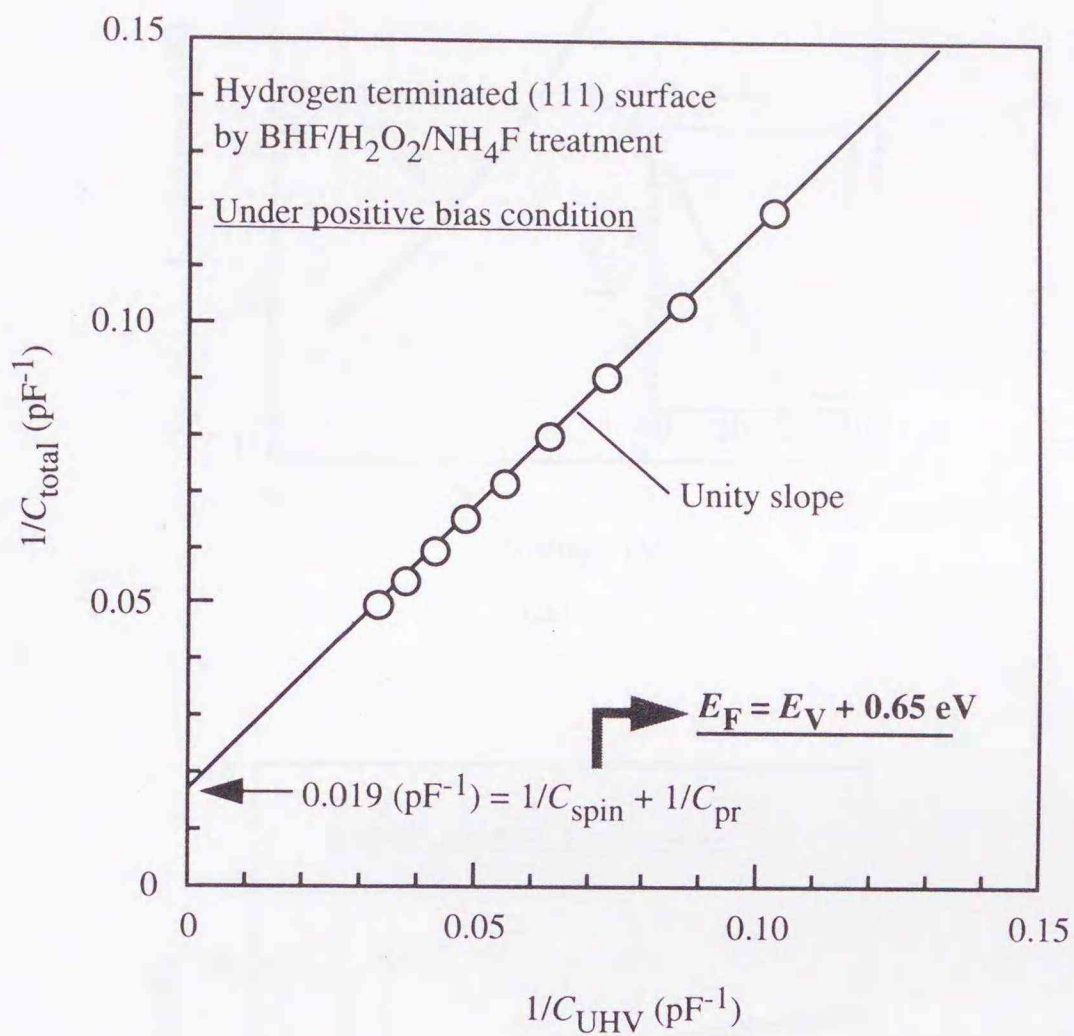


Fig. 4-6 Measured $1/C_{\text{total}}$ vs $1/C_{\text{UHV}}$ plot for hydrogen terminated Si (111) surface prepared by BHF/H₂O₂/NH₄F treatment under positive bias condition.

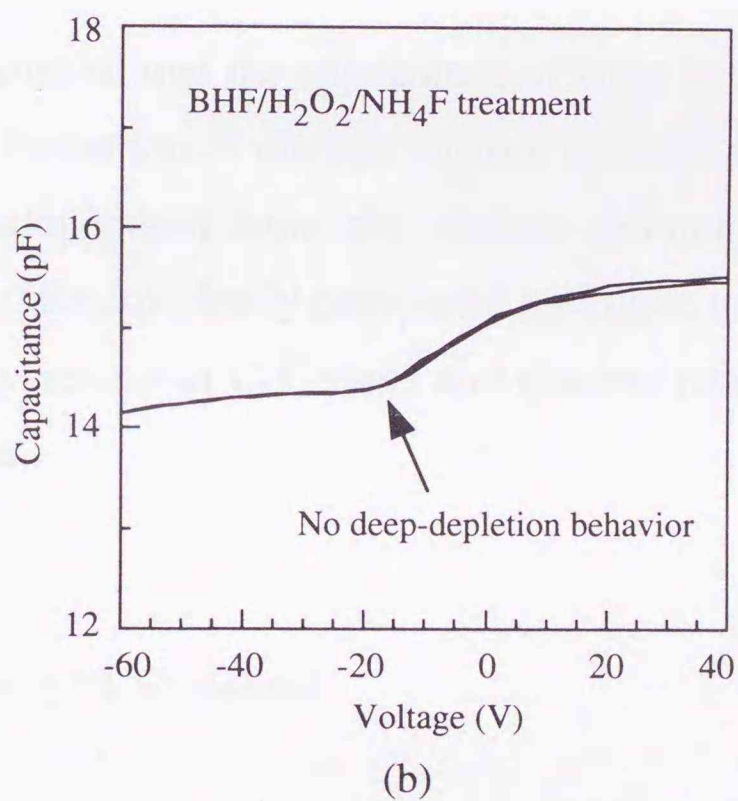
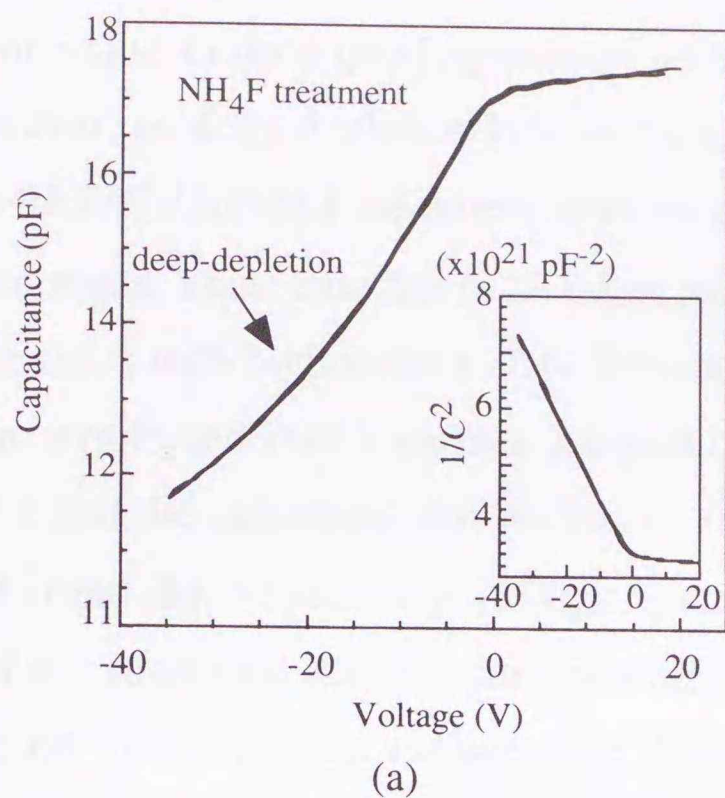


Fig. 4-7 UHV contactless C - V curves of hydrogen terminated (111) surfaces prepared by (a) NH_4F treatment and (b) $\text{BHF}/\text{H}_2\text{O}_2/\text{NH}_4\text{F}$ treatment, respectively, measured in pulsed bias mode. The inset shows the $1/C^2$ - V plot, which indicated that the conduction type and carrier concentration values show good agreement with those from Hall measurements.

curve obtained on the hydrogen terminated surface by NH_4F treatment, and the carrier concentration value showed good agreement with that obtained from the Hall measurement. However, no deep depletion behavior could be seen in the C - V curve of the surface after $\text{BHF}/\text{H}_2\text{O}_2/\text{NH}_4\text{F}$ treatment obviously due to the rapid response of high-density surface states. Thus, care has to be taken for the determination of doping concentration on surfaces with high surface state densities.

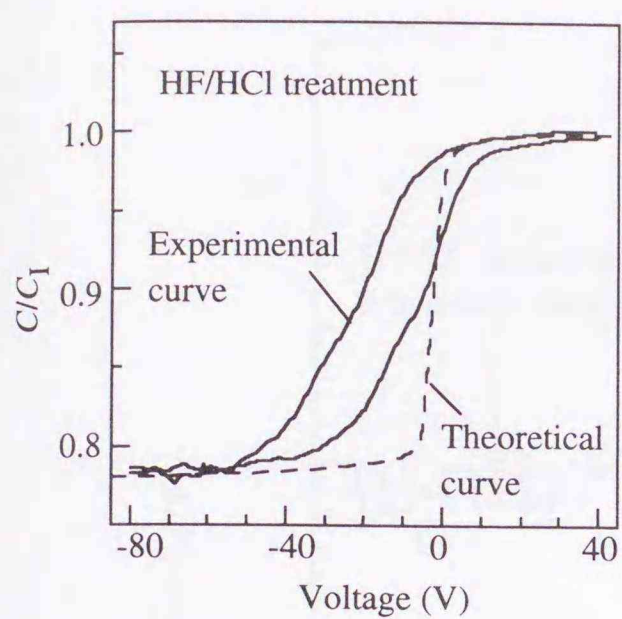
For hydrogen terminated (001) surface prepared by HF/HCl treatment, the measured C - V curve and the calculated distribution of surface state density (N_{ss}) are shown in **Fig. 4-8 (a)** and **(b)**, respectively. A large hysteresis with clock-wise loop in the C - V curve, and the additional discrete surface state peak at around 0.65 eV from valence band edge on the calculated surface state density distribution, were again detected. These phenomena are very similar to hydrogen terminated (111) surfaces described above.

So, it is considered that the appearance of large hysteresis with clock-wise loop in C - V curve and formation of discrete surface states at around 0.65 eV from valence band edge are independent from the surface orientation and treatment method. Anyway, for realization of ideally passivated hydrogen terminated Si surface, it needs to remove these hysteresis in C - V curve and discrete peak at around 0.6-0.7 eV from valence band edge.

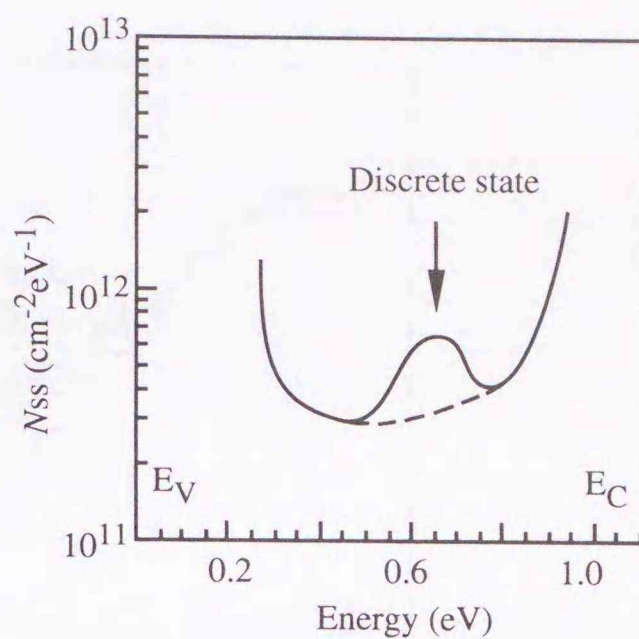
4.3.4 Analysis using PLS³ method

To further investigate the properties of hydrogen terminated Si surface, photoluminescence surface state spectroscopy (PLS³) measurement was performed. **Figure 4-9** shows the measured relationship between the PL efficiency and excitation intensity for the hydrogen terminated Si surface prepared by $\text{BHF}/\text{H}_2\text{O}_2/\text{NH}_4\text{F}$ treatment. The result obtained from high-temperature thick thermal oxide covered Si surface was also shown as a reference, and the PL efficiency was normalized by that of the highest excitation level.

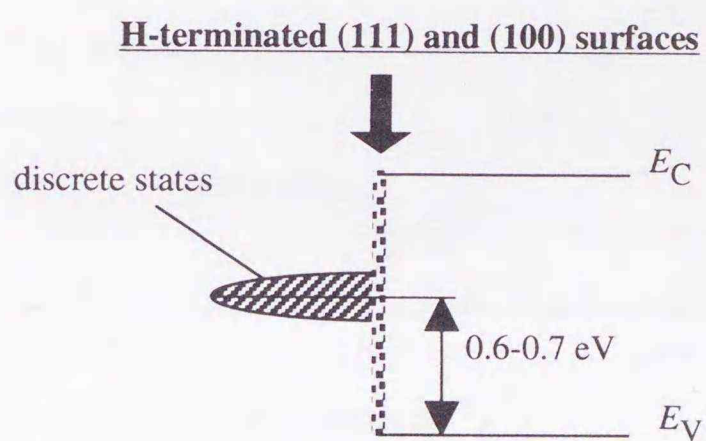
The hydrogen terminated surface prepared by $\text{BHF}/\text{H}_2\text{O}_2/\text{NH}_4\text{F}$ treatment gave



(a)



(b)



(c)

Fig. 4-8 (a) UHV contactless C - V curve of hydrogen terminated (100) surface prepared by HF/HCl treatment and (b) a calculated N_{ss} distribution using Terman's method. A model of surface state distribution of hydrogen terminated (111) and (100) surfaces are written in (c).

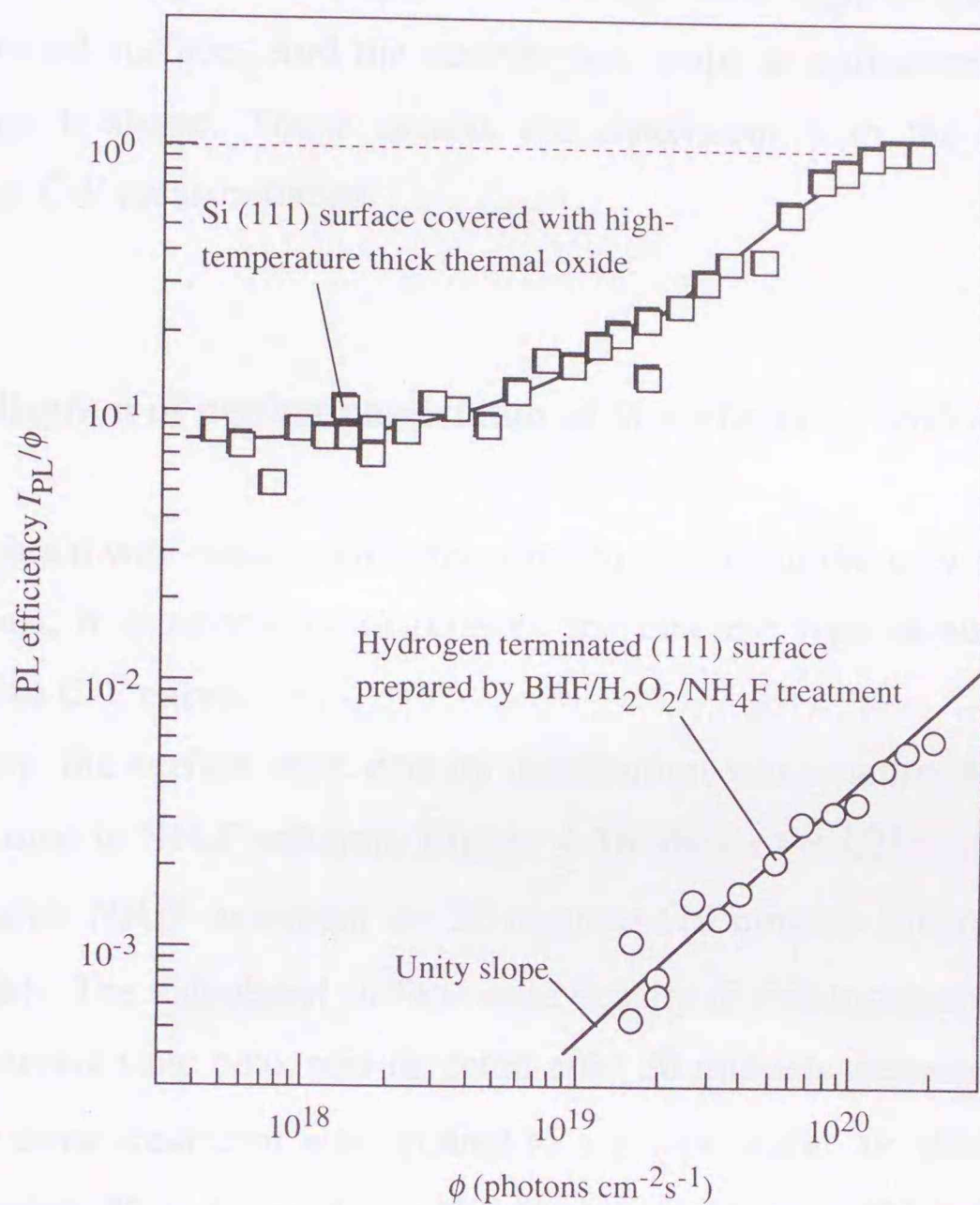


Fig. 4-9 The measured relationship between the PL efficiency and excitation intensity for the hydrogen terminated surface prepared by BHF/H₂O₂/NH₄F treatment. The result obtained from high-temperature thick thermal oxide covered surface is also shown as a reference.

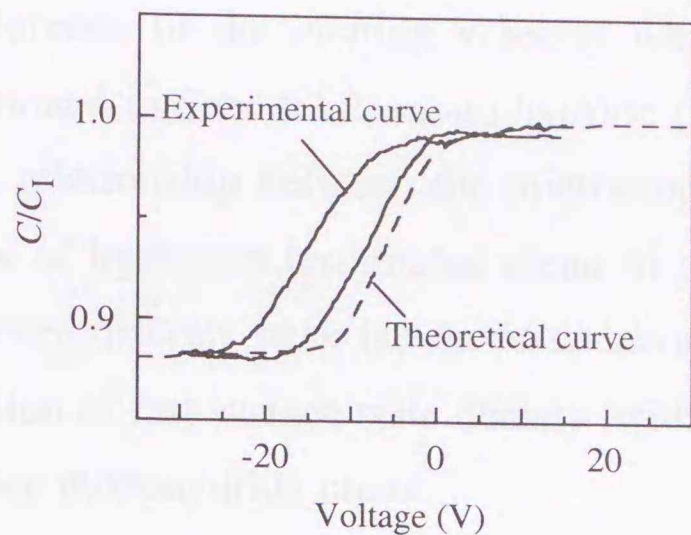
very low PL efficiencies where the slope of the PL efficiency vs excitation intensity was unity. These results indicate that surface states exist on this surface which density is much higher than that of well-passivated high-temperature thick thermal oxide covered surface. And the distribution shape is a discrete shape rather than a continuous U-shape. These results are consistent with the results of XPS and contactless C - V measurements.

4.4 Realization of perfect passivation of Si surfaces by hydrogen atoms

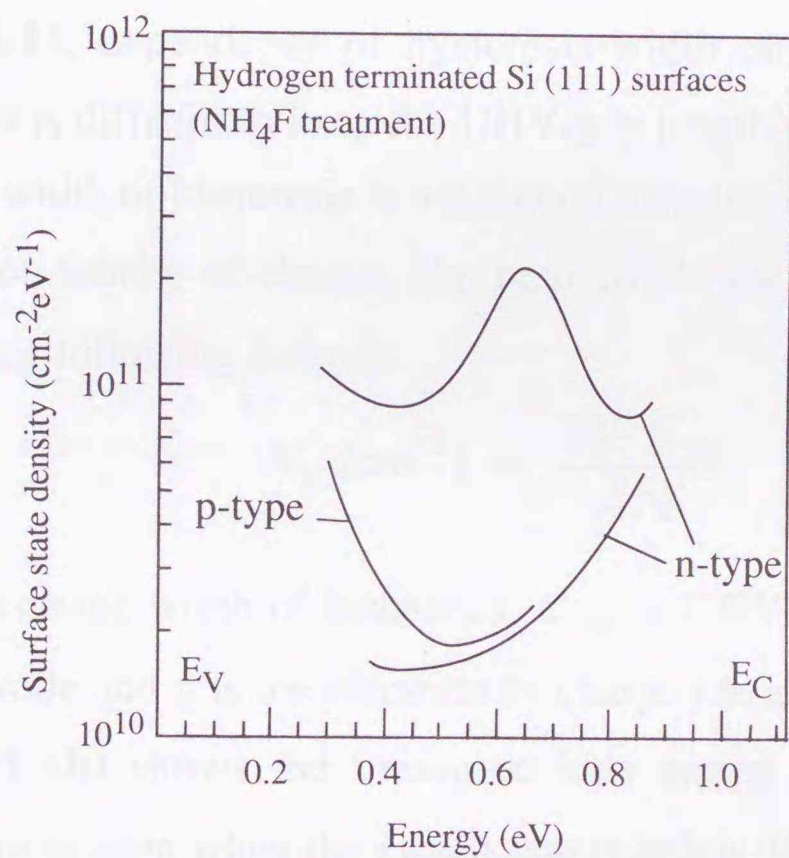
To obtain well-passivated defect-free Si surface in the view of device processing applications, it is necessary to remove the discrete type of surface states and the hysteresis in C - V curve.

Firstly, the surface state density distribution was examined as a function of the treatment time in NH_4F solution. **Figure 4-10** shows the UHV contactless C - V curve obtained after NH_4F treatment for 30 minutes (10 minutes longer than that shown in **Fig. 4-5 (b)**). The calculated surface state density distributions are shown in **Fig. 4-10 (b)**. No discrete state peak was detected after 30 minutes treatment in NH_4F solution. When the same treatment was applied to a p-type wafer, no discrete state peak was detected either. Thus, by applying NH_4F treatment for a sufficiently long time, the fast states having a discrete peak at 0.6-0.7 eV above valence band edge can be suppressed. The minimum value of surface state density also reduced down to $1\text{-}2 \times 10^{10} \text{ cm}^{-2}\text{eV}^{-1}$ which is comparable to those for well passivated surface covered with a high temperature thick thermal oxide.

The above result suggest that hydrogen-termination by monohydride phase is a slow process. It is known that the surface Si atoms are etched slowly by NH_4F solution. A thermal-desorption-spectroscopy (TDS) study^{28,29} has shown that the (111) surface treated for short time by NH_4F solution has complicated hydride phases such as Si-H_2 or Si-H_3 . But these phases reduced with extending the treatment time in NH_4F solution. Other group²⁵ reported that the Si (111) surface is etched and



(a)



(b)

Fig. 4-10 (a) Measured UHV contactless C - V curve and (b) calculated surface state density distributions obtained from hydrogen terminated (111) surface treated in NH_4F solution. The treatment time in NH_4F solution ranged from 20 to 30 min.

flattened, then eventually completely covered with a stable monohydride layer because of the difference of the etching velocity which depends on the surface orientation (as mentioned in Sec. 4.3.2, mono-hydride (111) surface is most stable). Although a definite relationship between the microscopic surface structure and the electronic properties of hydrogen terminated clean Si surfaces has not been established yet, the observed discrete peak is related to incompleteness of mono-hydride phase and the reduction of fast surface state density with time seems to reflect such a stabilization of surface monohydride phase.

On the other hand, after removal of discrete states, the large hysteresis in C - V curve still remained (as shown in **Fig. 4-10 (a)**). Here, removal of this hysteresis is required to realize a perfect passivation of Si surface utilizing hydrogen termination. Firstly, in **Fig. 4-11**, dependence of hysteresis-width on the bias sweep-rate was examined. Since it is difficult to keep the UHV-gap length the same in each measurement, the voltage width of hysteresis is not a good measure for comparison. Therefore, the surface number density of charge, N_H , responsible for hysteresis was calculated and compared using following formula.

$$N_H [\text{cm}^{-2}] = \frac{\Delta V \cdot C_{\text{gap}}}{S \cdot q} \quad (4-1)$$

where ΔV is the voltage width of hysteresis, C_{gap} is UHV-gap capacitance, S is the area of field electrode and q is the elementary charge (details are shown in **Fig. 4-11 (a)**). **Figure 4-11 (b)** shows the measured bias sweep rate dependence of N_H . Saturation behavior is seen when the sweep rate is below 1 V/sec, indicating that the present charge instability phenomenon can follow such a sweep speed. Namely, it needs to compare the value of N_H at the bias sweep-rate less than 1 V/sec.

Then, the surface number density of charge N_H was examined as a function of additional annealing temperature in UHV environment. The diagram of infrared radiation (IR) heating system is schematically shown in **Fig. 4-12**. The UHV annealing chamber had an infrared radiation heating system (GVH298, THERMO RIKO Co., Ltd.) where the infrared radiation was transmitted from the heating source on the atmospheric side through a gold spheroidal mirror and a quartz rod. The sample can

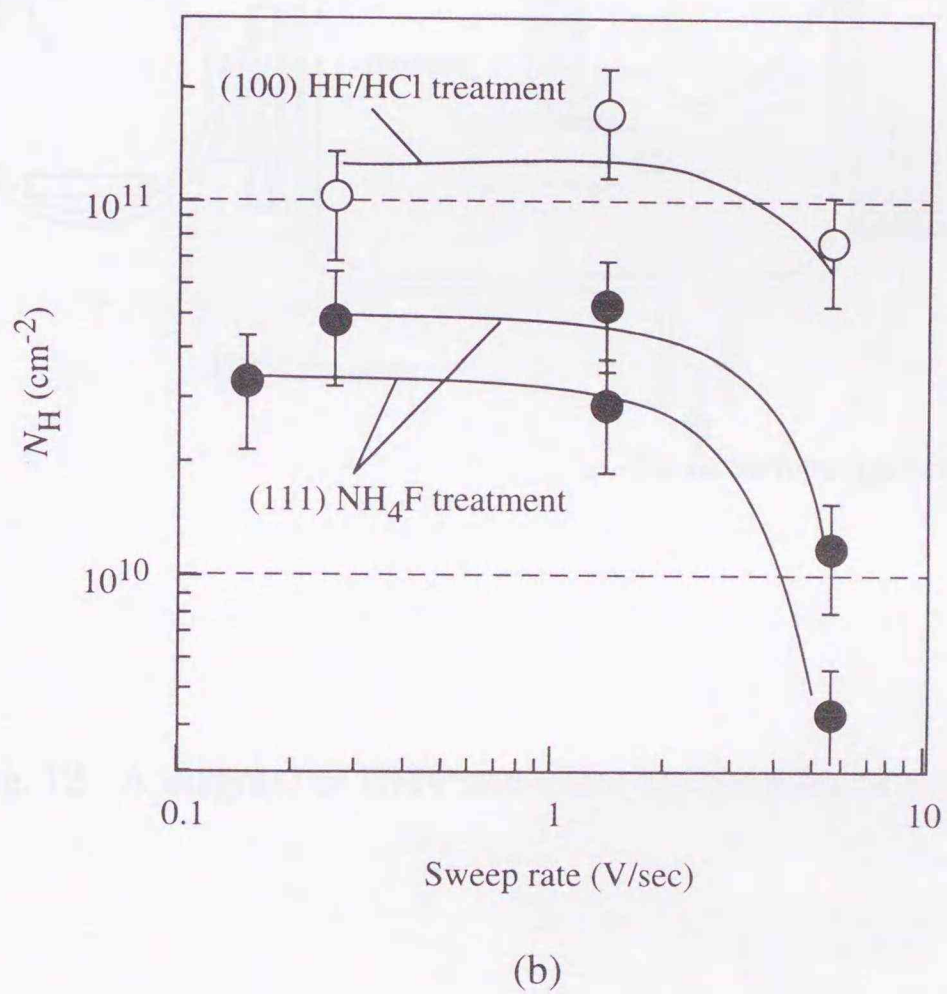
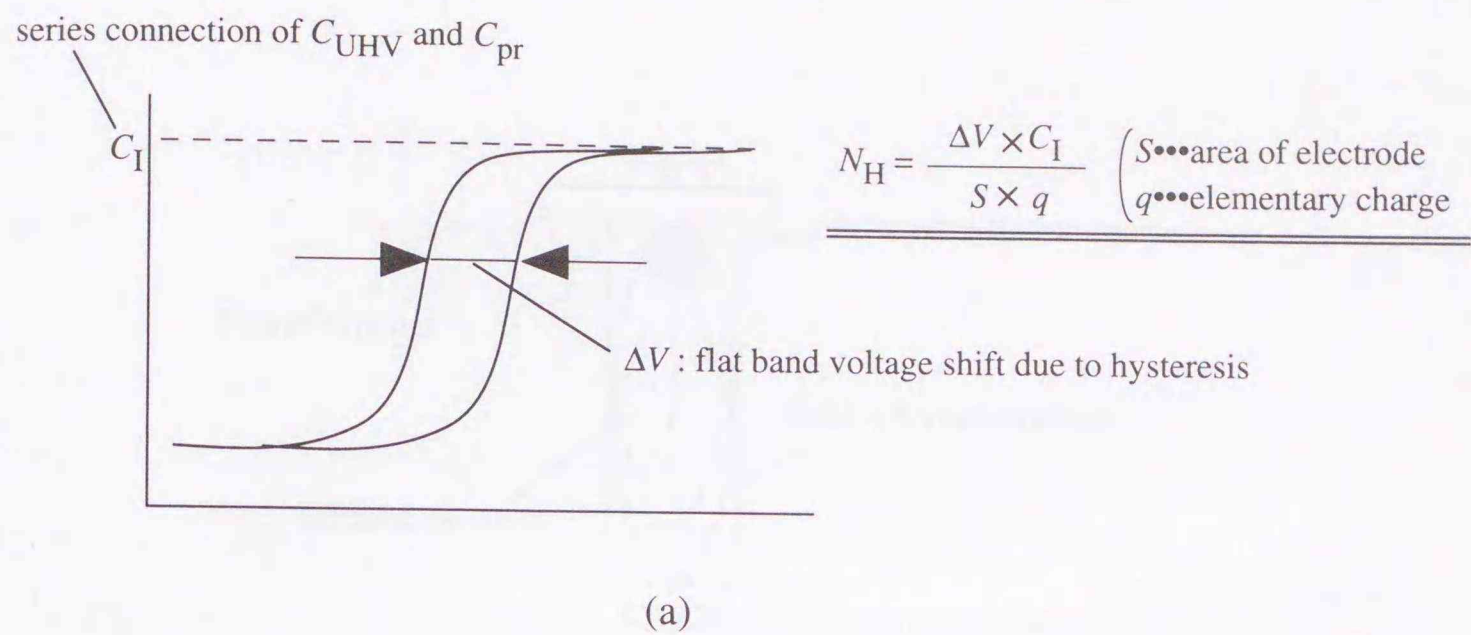


Fig. 4-11 (a) The calculation method hysteresis charge density (N_H) and (b) measured bias sweep-rate dependence of N_H .

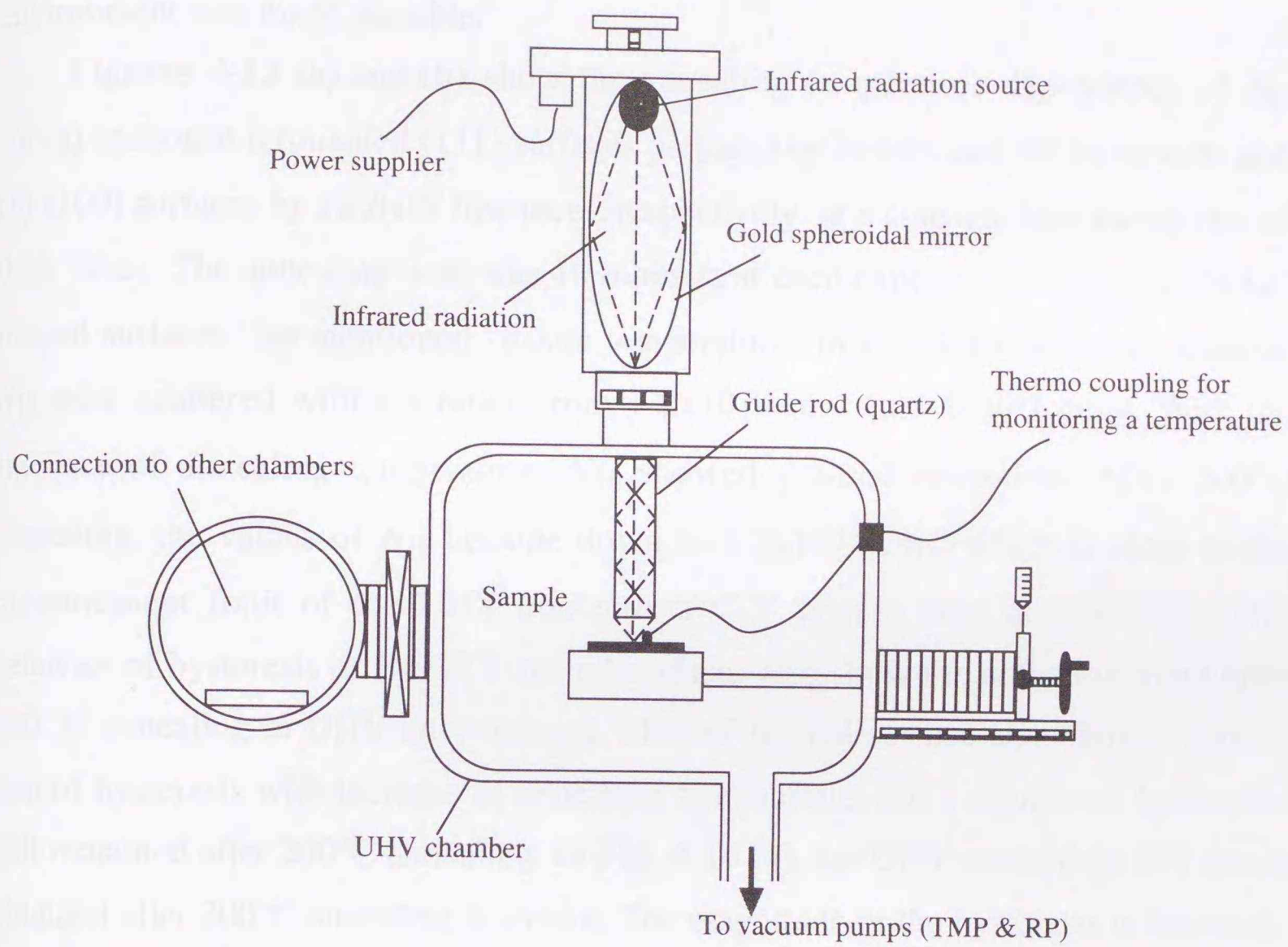


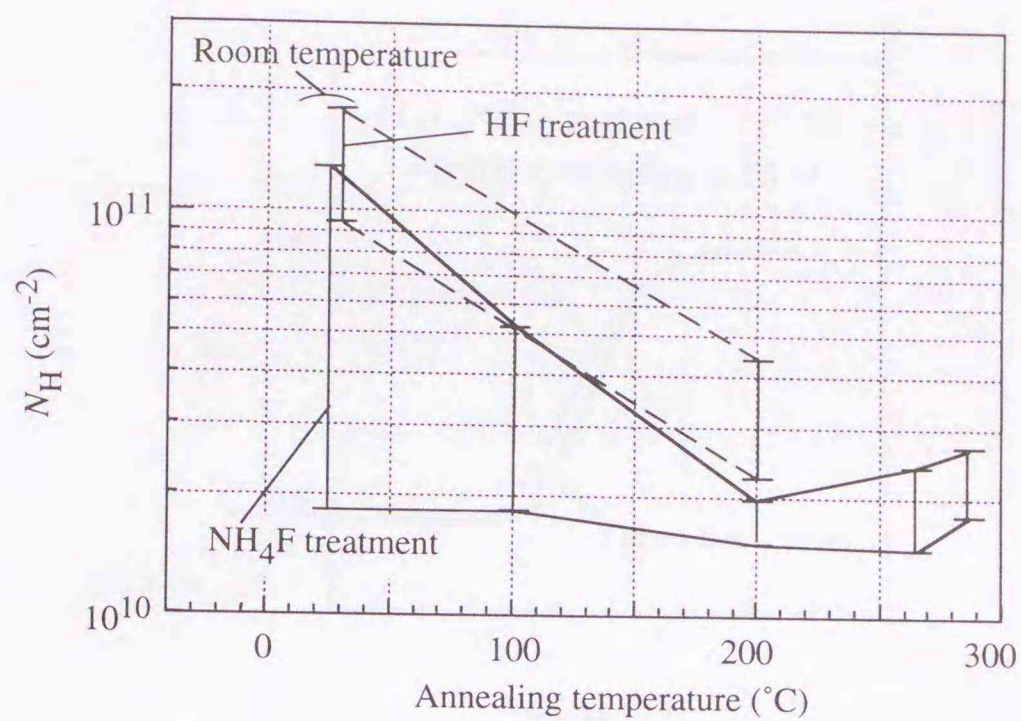
Fig. 12 A diagram of UHV annealing system with IR heating system

be transferred from UHV-transfer-tunnel in UHV-multi-chamber-system described in Chapter 3, and is moved underneath the quartz rod. The base pressure of this chamber was 3×10^{-10} Torr and therefore annealing of the surface in an ultraclean environment was made possible.

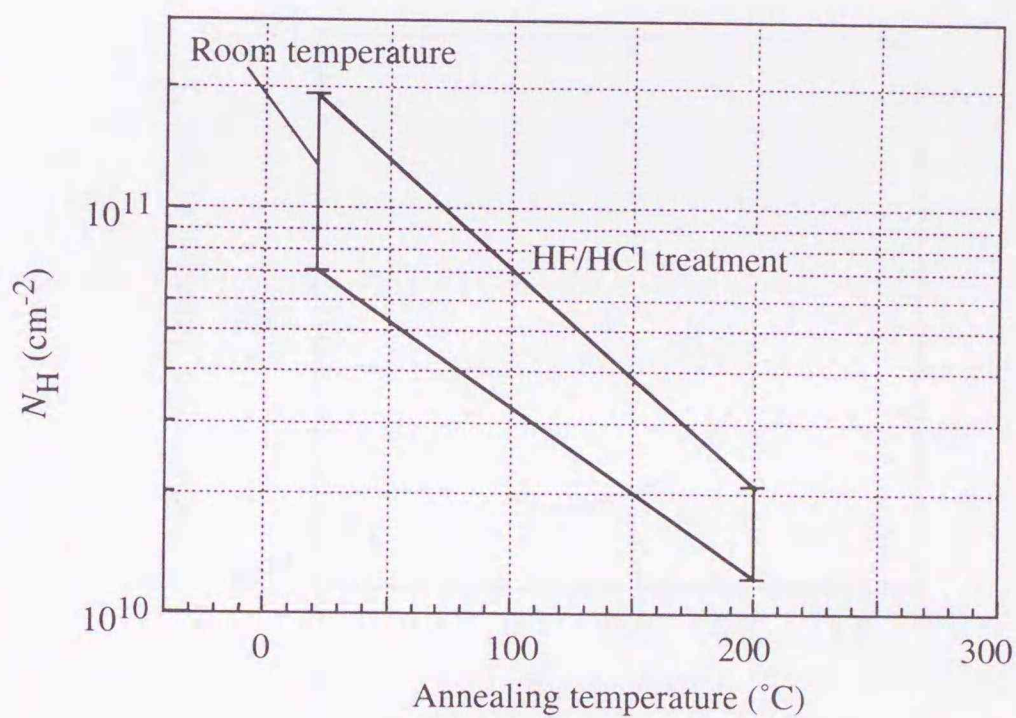
Figures 4-13 (a) and (b) show the annealing temperature dependence of N_H for (a) hydrogen terminated (111) surfaces prepared by NH_4F - and HF treatments and (b) (100) surfaces by HF/HCl treatment, respectively, at a constant bias sweep rate of 0.15 V/sec. The annealing time was 10 minutes at each experiment. On the as- NH_4F treated surfaces (as mentioned "Room temperature" in **Fig. 4-13 (a)**), the values of N_H were scattered within a range from $1-2 \times 10^{10} \text{ cm}^{-2}$ to $1-2 \times 10^{11} \text{ cm}^{-2}$. With the increase of annealing temperature, N_H showed gradual reduction. After 200°C annealing, the values of N_H became down to $1-2 \times 10^{10} \text{ cm}^{-2}$ which is close to the measurement limit of the UHV contactless C - V system used in this study. The behavior of hysteresis of HF/HCl treated surfaces also show the reduction trend after 200°C annealing in UHV environment. The HF treated surface also showed reduction of hysteresis with increase of annealing temperature, but a significant hysteresis still remained after 200°C annealing. In **Fig. 4-14 (a)**, the UHV contactless C - V result obtained after 200°C annealing is shown. The magnitude of the hysteresis is drastically reduced. On the other hand, the surface state density distribution showed almost same shape before and after the annealing, i.e. the wide U-shaped distribution and the minimum value of $1-2 \times 10^{10} \text{ cm}^{-2}\text{eV}^{-1}$ (as shown in **Fig. 4-14 (b)**).

Thus a UHV-compatible perfect passivation can be realized by an optimal hydrogen termination process; combined use of the enough time treatment in NH_4F solution and annealing at 200°C in UHV environment.

Here, the possible origin of the hysteresis in measured C - V curve is discussed. Generally, C - V hysteresis is caused by ion movement or by charge-discharge transients of slow surface states. However, since movable vertical distance of adsorbed ion species is much smaller than the UHV-gap width, the ion instability is very unlikely. Furthermore, the C - V curves measured here showed clock-wise loops rather

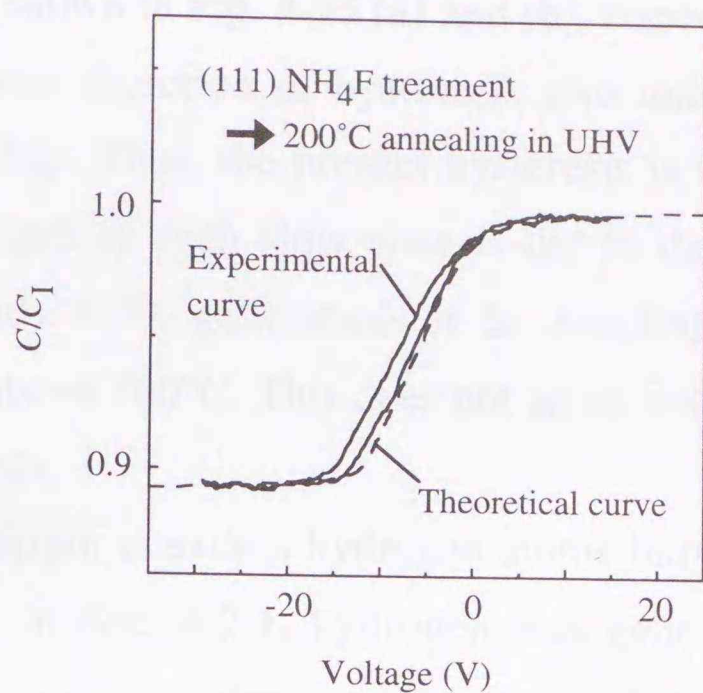


(a) (111) surfaces

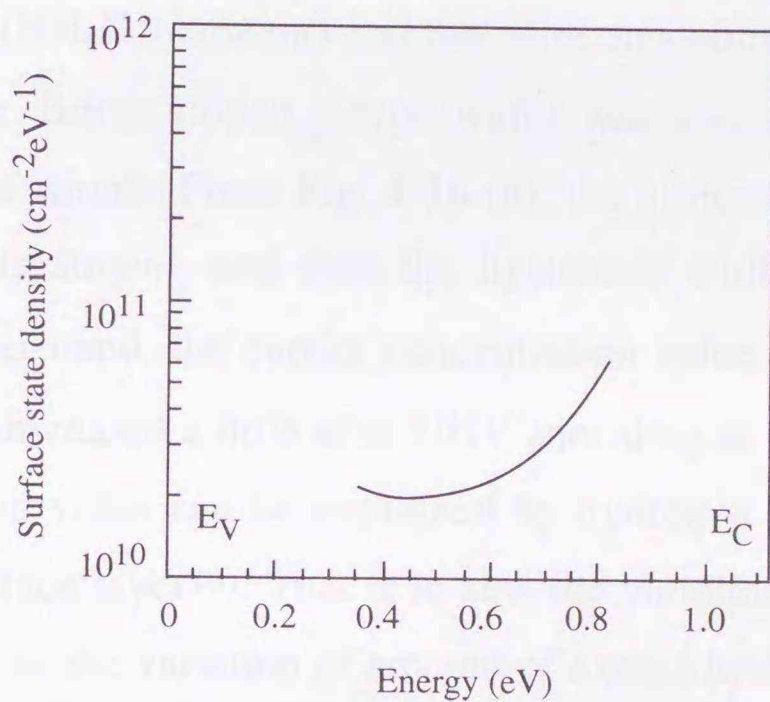


(b) (100) surfaces

Fig. 4-13 The measured annealing temperature dependence of the hysteresis charge density (N_H) for hydrogen terminated (a) (111) and (b) (100) surfaces.



(a)



(b)

Fig. 4-14 UHV contactless C - V curve obtained from NH_4F treated surface after 200°C annealing in UHV environment. The annealing time was 10 min.

than anti-clock-wise loops. The explanation of the clock-wise and anti-clock-wise loops are schematically shown in Fig. 4-15 (a) and (b), respectively. As mentioned in Sec. 2.3.2, the clock-wise direction of hysteresis also indicates the denial of the existence of ion instability. Thus, the present hysteresis is more likely due to slow states. One possible origin of such slow state is the Si dangling bond. However, according to TDS study^{28,29)}, generation of Si dangling bond due to H atom desorption takes place above 260°C. This does not agree with the observed temperature behavior of hysteresis.

Another possible origin is excess hydrogen atoms introduced in wet chemical process. As mentioned in Sec. 4.2.1, hydrogen was generated in NH_4F etching process. Here, an interesting coincidence can be seen in Fig. 4-16. In this figure, the hysteresis width in C-V curve and the measured carrier concentration value are shown for the surface covered with high temperature thick thermal oxide, that after hydrogen termination (NH_4F treatment) and that after annealing in UHV environment at 200 °C for 10 min. Boron doped p-type wafer was used, and all of data were obtained from the same sample. From Fig. 4-16 (a), the hysteresis was appeared in C-V curve after NH_4F treatment, and then the hysteresis width decreased by UHV annealing. On the other hand, the carrier concentration value decreased after NH_4F treatment, and then it increased a little after UHV annealing at 200 °C. This reduction of carrier concentration value can be explained by hydrogen passivation of dopant (boron) atoms in a surface layer¹³⁾. That is to say, the variation of carrier concentration value corresponds to the variation of amount of excess hydrogen atoms; increase of carrier concentration value corresponds to decrease of excess hydrogen atoms, and decrease of carrier concentration value corresponds to increase of excess hydrogen atoms. Here, the term *excess hydrogen* means the hydrogen atoms which exist at/near the surface and do not contribute to terminate the Si dangling bond. So, the hysteresis behavior in C-V curve shows good agreement with the amount of excess hydrogen. It is not yet clear about the detail kinetics to create the slow state using excess hydrogen atoms, however, it will be said that the most likely origin of the slow surface states causing hysteresis is excess hydrogen atoms³⁰⁾ which has been shown to disappear after 200 °C annealing in UHV environments.

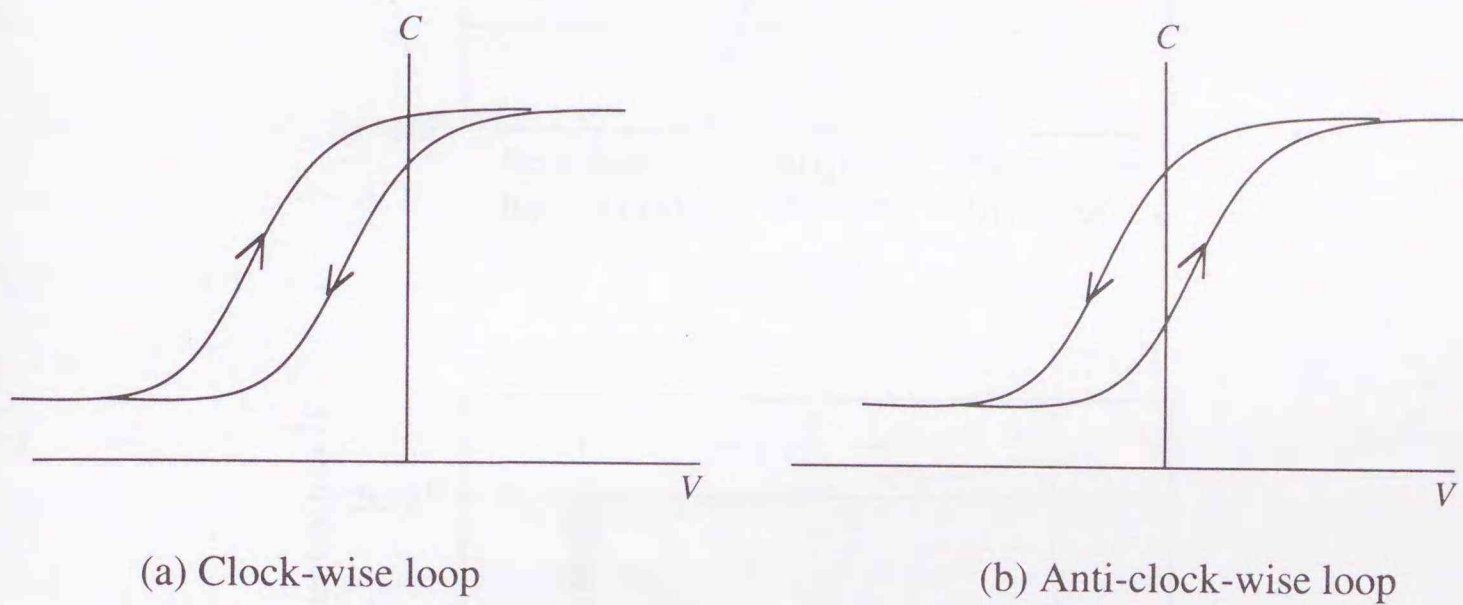


Fig. 4-15

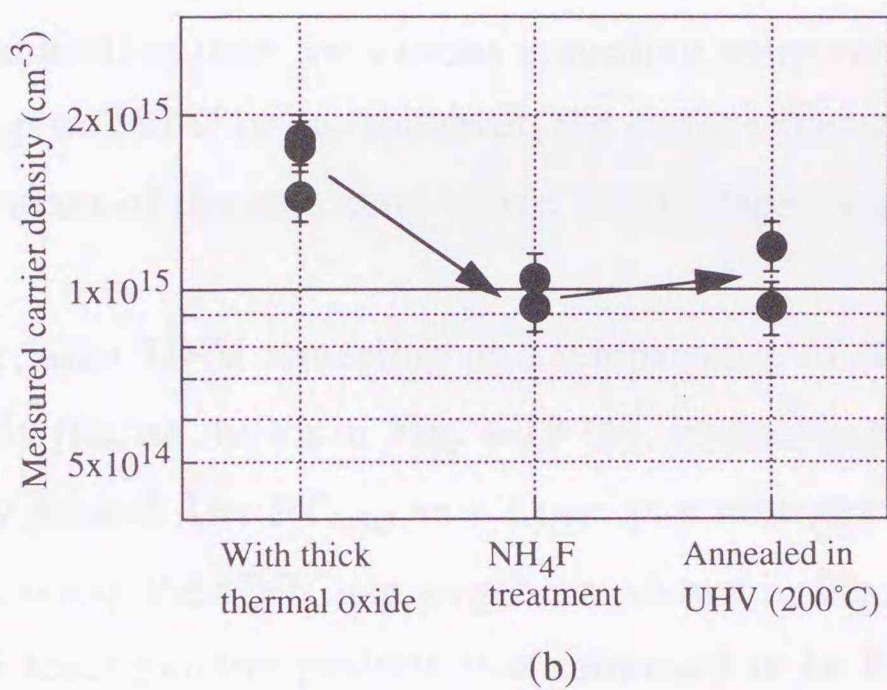
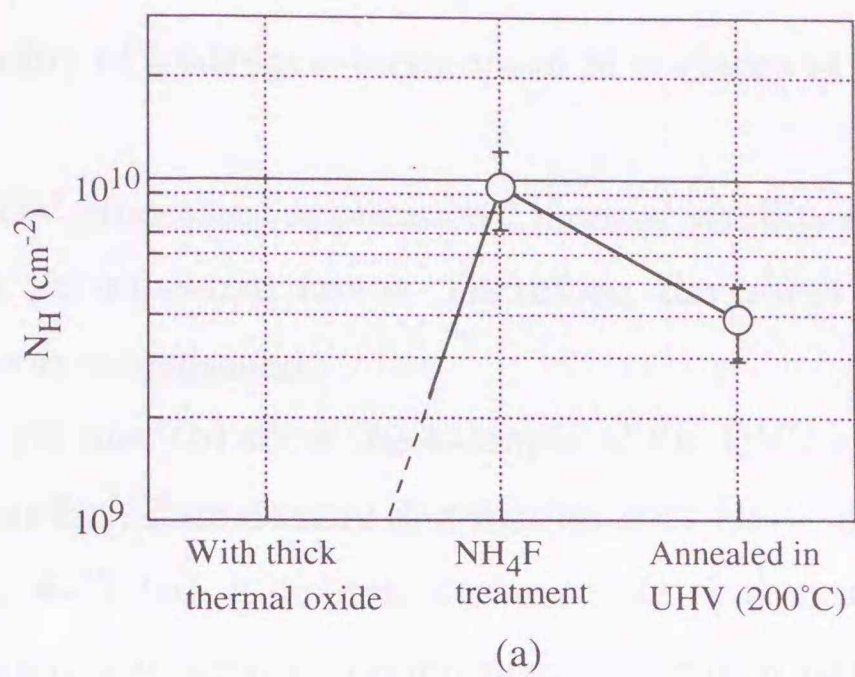


Fig. 4-16 Measured (a) N_H values and (b) carrier densities for p-type Si(111) surfaces after high temperature thermal oxidation, hydrogen termination (NH_4F treatment) and annealing in UHV environment (200°C). These data were obtained from the same sample.

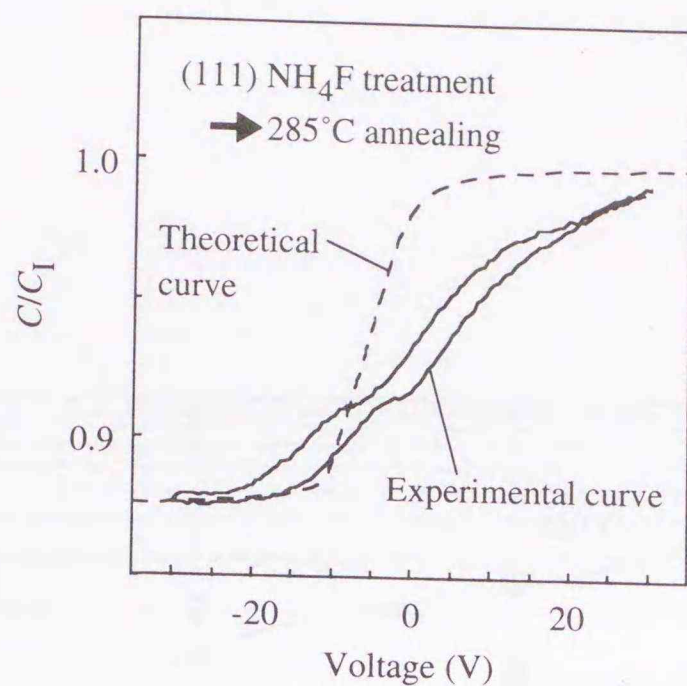
4.5 Thermal stability of hydrogen-terminated Si surfaces in UHV environment

For various UHV processing applications, thermal stability of the well-passivated surface in UHV is an important factor. Therefore, the effect of high temperature annealing in UHV was investigated.

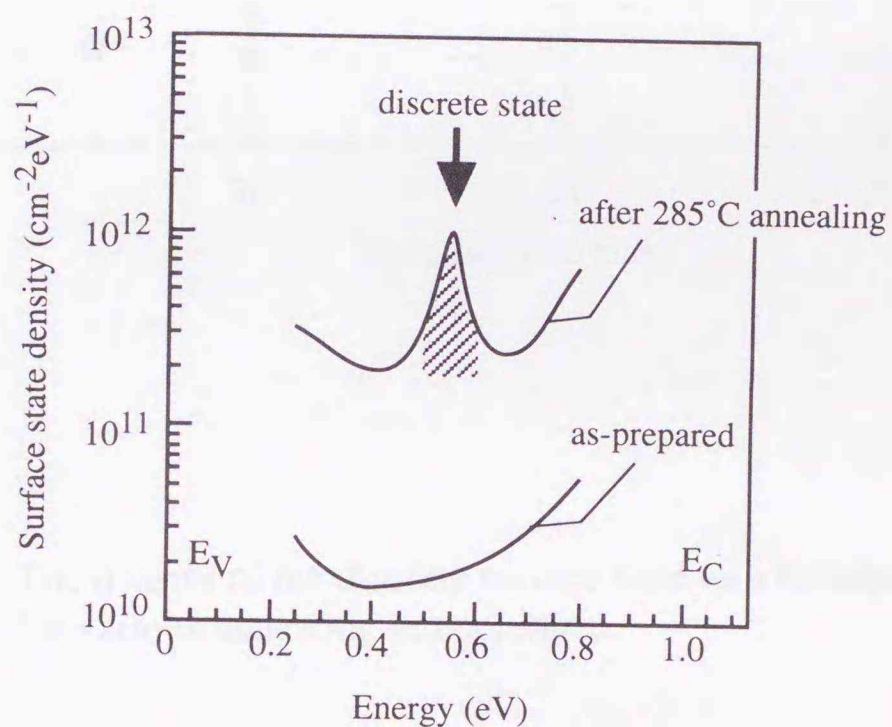
Figures 4-17 (a) and (b) show the example of the UHV contactless C-V curve and the calculated surface state density distribution after UHV annealing at 285°C for 30 minutes. In **Fig. 4-17 (b)**, a discrete surface state peak near the midgap clearly appeared again which was seen in unoptimized hydrogen terminated surfaces (as shown in **Figs. 4-5 (d) and 4-8 (b)**). **Figure 4-18** shows the density of discrete state as a function of annealing time for various annealing temperature. The surface was thermally stable up to 250°C or so. However, the surface started to show appearance of appreciable amount of discrete state above 250°C depending also on the annealing time.

Furthermore, after UHV annealing at a temperature of 500°C, the C-V curve became completely flat, as shown in **Fig. 4-19 (a)**, indicating that the surface Fermi level was strongly pinned. The $1/C_{\text{total}}$ vs $1/C_{\text{UHV}}$ plot obtained from the capacitance measurements changing the UHV gap length are shown in **Fig. 4-19 (b)**. Using Eq. (3-17), the Fermi level pinning position was estimated to be $E_V + 0.65$ eV, and this position is the same as that of the discrete surface states existing on as-treated and on annealed hydrogen terminated surfaces mentioned above.

These data also provides a clue as regards the origin of the discrete state peak. According to a recent TDS study, hydrogen desorption starts at about 260°C and increases rapidly with temperature (a copy of TDS spectra reported by other workers²⁹⁾ is shown in **Fig. 4-20**). From this figure, at the temperature ranged less than 300 °C, desorption of hydrogen atoms at di- and tri-hydride phases occurred, and the hydrogen atoms at mono-hydride phase which mainly existed on the terrace part of the surface started to desorb at the temperature of higher than 300 °C. Finally, above 500 °C, almost of hydrogen atoms were removed. The desorption of hydrogen



(a)



(b)

Fig. 4-17 (a) UHV contactless C - V curve and (b) calculated surface state density distribution from NH_4F treated surface after annealing in UHV environment. The annealing temperature was 285°C and the annealing time was 30 min.

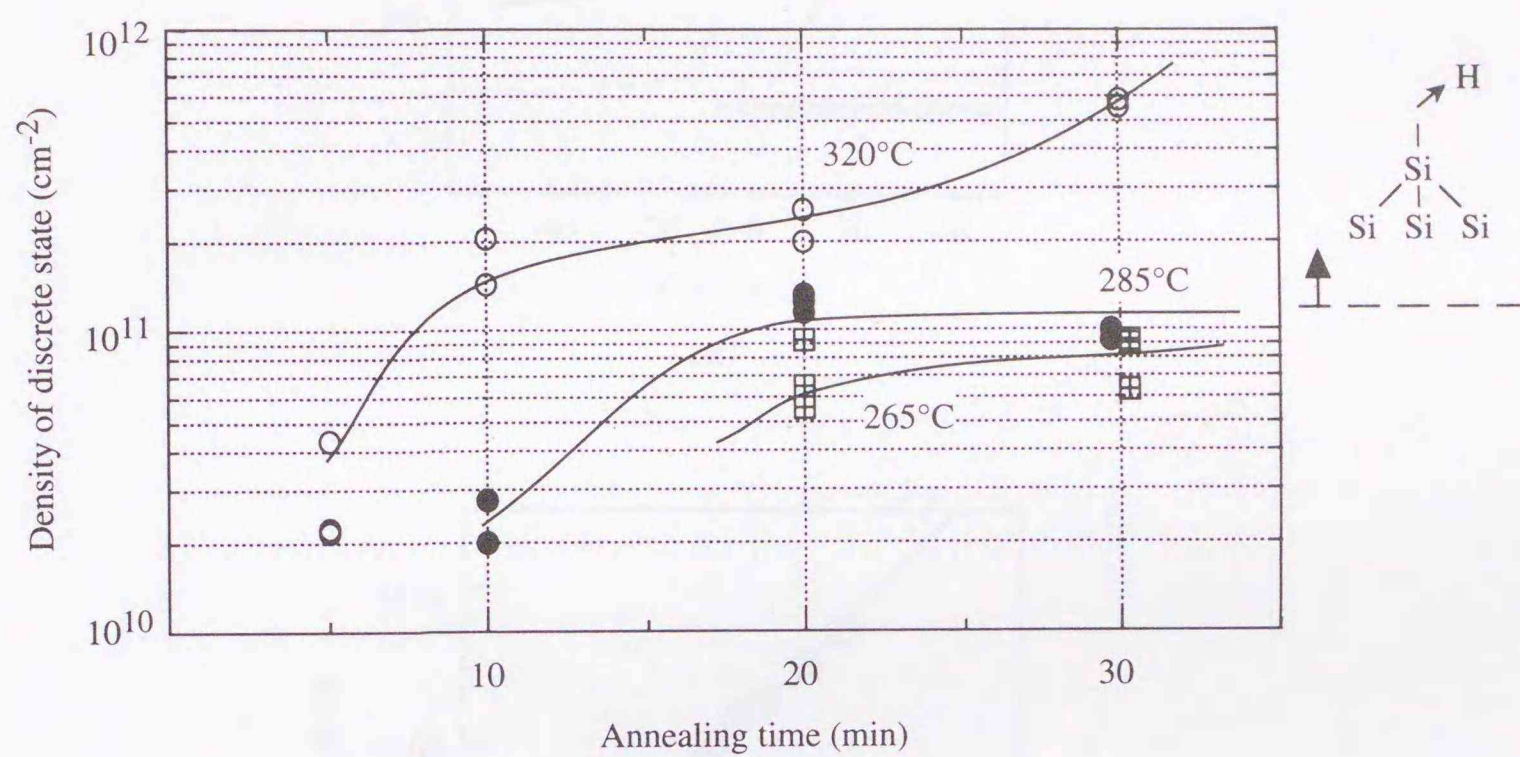


Fig. 4-18 The density of the discrete surface state as a function of annealing time for various annealing temperatures.

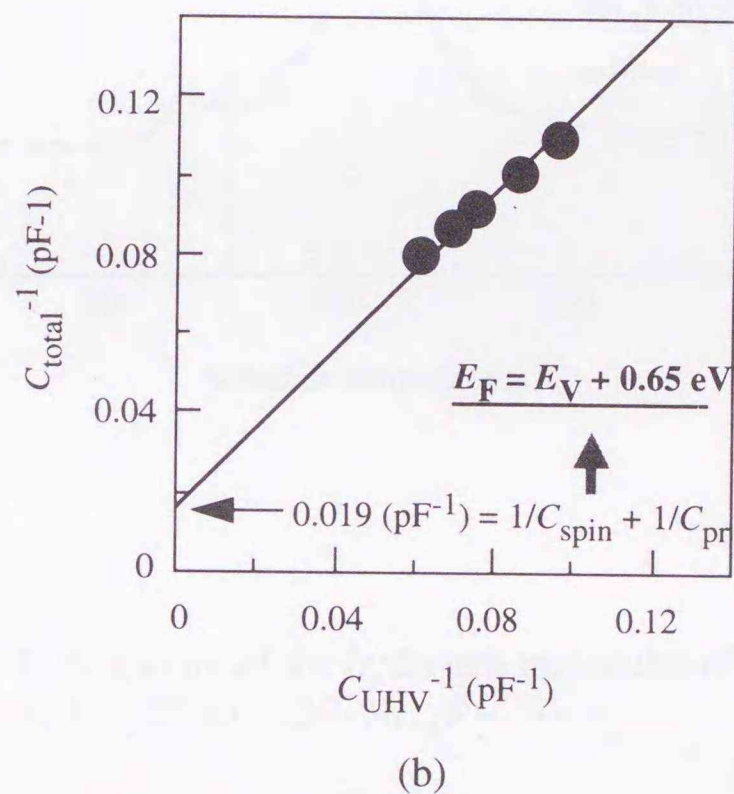
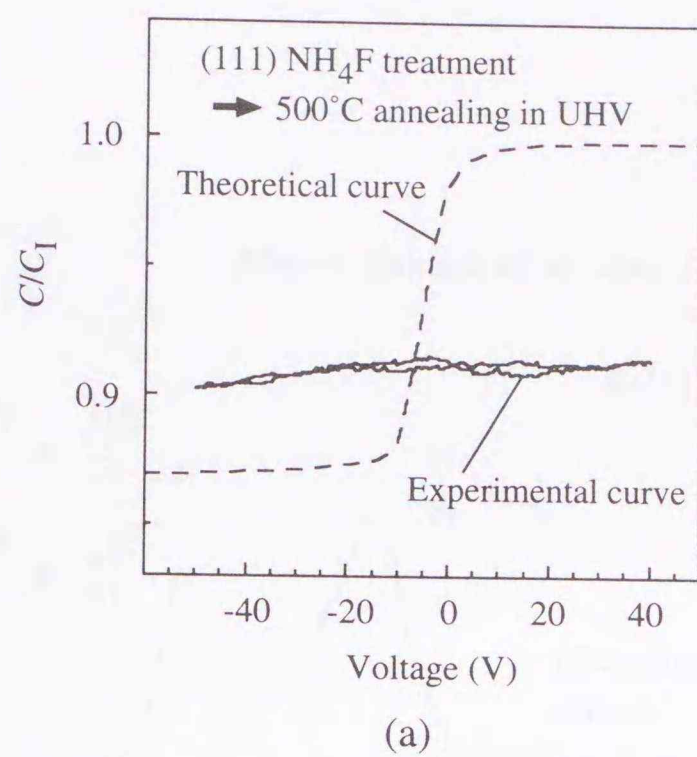


Fig.4-19 (a) UHV contactless C - V curve of hydrogen terminated (111) surface treated in NH_4F solution after 500°C annealing in UHV environment and (b) the $1/C_{\text{total}}$ vs $1/C_{\text{UHV}}$ plot indicating the Fermi level pinning position of 0.65 eV from valence band edge.

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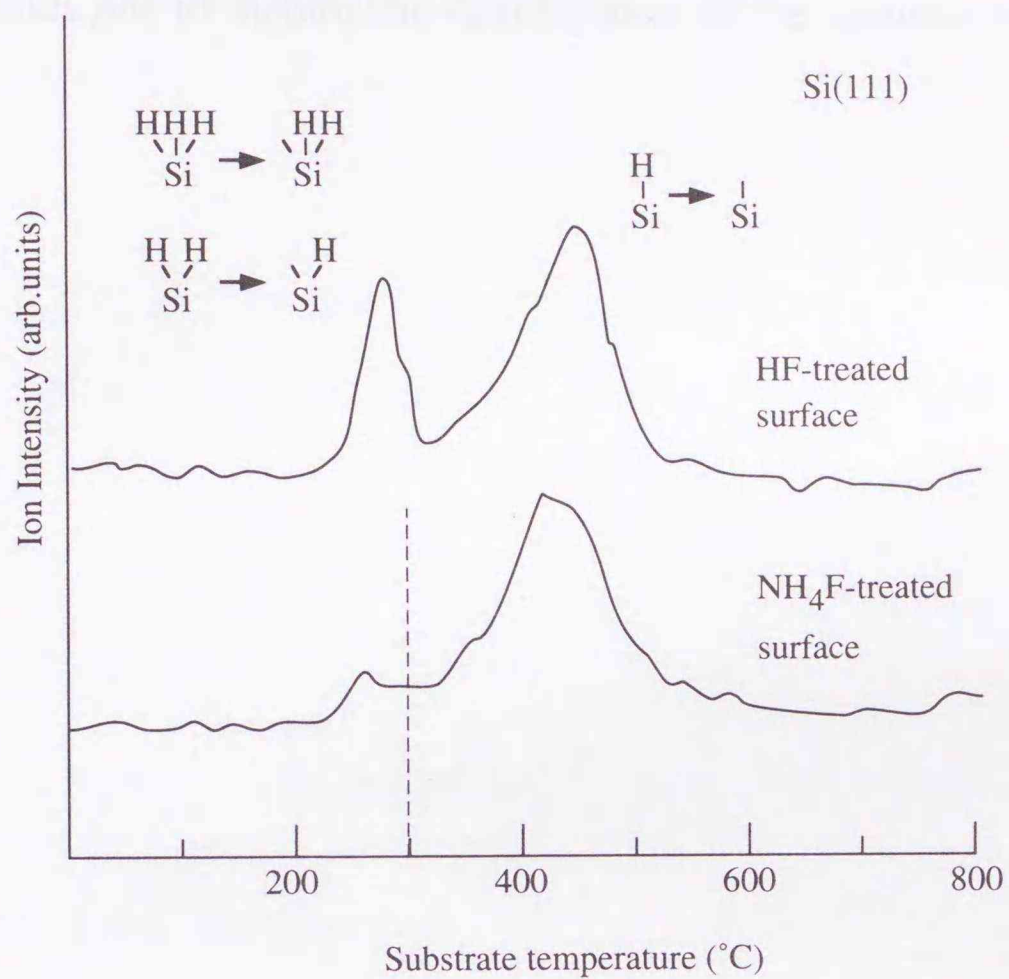


Fig. 4-20 TDS spectra of the hydrogen molecules of Si(111) wafers treated by 5% HF and 40% NH₄F.

atoms creates Si-dangling bonds, which act as electronically active defects and pin the surface Fermi level. Thus, the most likely origin of the fast surface state with a discrete peak at around 0.65 eV from valence band edge is due to Si-dangling bond. Incomplete passivation by short treatment time seems to result in presence of Si-dangling bonds due to incomplete development of the monohydride phase.

4.6 Summary

The hydrogen terminated Si surfaces were characterized using x-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM), ultrahigh-vacuum (UHV) contactless capacitance-voltage (*C-V*) method and photoluminescence surface state spectroscopy (PLS³). The main summaries are as follows.

- (1) By dipping the Si(111) wafer into NH_4F solution, atomically clean and flat surface with terrace-step structure could be obtained, while the surface became atomically roughened after the treatment in HF solution. The terrace-step pattern shows the variety depending on the light intensity or the treatment time in NH_4F solution.
- (2) Hydrogen terminated Si surfaces possess fast surface states which has a discrete peak at 0.6-0.7 eV from valence band edge. They also possess slow states which causes hysteresis in *C-V* curves.
- (3) By the sufficiently long NH_4F treatment, the discrete states disappeared, and the hysteresis in *C-V* curve drastically reduced after UHV anneal at 200 °C. Thus, a UHV-compatible completely passivated surface could be obtained. Such surface seems to be thermally stable up to 250°C.
- (4) The most likely origin of fast surface states is Si-dangling bond, and that of slow surface states is excess hydrogen.

References

- 1) Y. Morita, K. Miki and H. Tokumoto: Appl. Phys. Lett. **59** (1991) 1347.
- 2) D. Huang and Y. Yamamoto: Jpn. J. Appl. Phys. **35** (1996) 3734.
- 3) C. J. Karlsson, F. Owman: E. Landemark, Y. -C. Chao, P. Martensson and R. I. G. Uhrberg, Phys. Rev. Lett. **72** (1994) 4145.
- 4) C. H. Bjorkman, J. L. Alay, H. Nishimura, M. Fukuda, T. Yamazaki and M. Hirose: Appl. Phys. Lett. **67** (1995) 2049.
- 5) K. Hricovini, et. al.: Phys. Rev. Lett. **70** (1993) 1992.
- 6) Y. J. Chabal, G. S. Higashi, K. Raghavachari and V. A. Burrows: J. Vac. Sci. Technol. **A7** (1989) 2104.
- 7) C. C. Williams, W. P. Hough and S. A. Rishton: Appl. Phys. Lett. **55** (1989) 203.
- 8) C. C. Williams, J. Slinkman, W. P. Hough and H. K. Wickramasinghe: Appl. Phys. Lett. **55** (1989) 1662.
- 9) H. Tomiye, H. Kawami, M. Izawa, M. Yoshimura and T. Yao: Jpn. J. Appl. Phys. **34** (1995) 3376.
- 10) H. Tomiye, T. Yao, H. Kawami and T. Hayashi: Appl. Phys. Lett. **69** (1996) 4050.
- 11) T. Tagawa and T. Okumura: Solid-State Phenomena **65-66** (1999) 211.
- 12) A. K. Henning, T. Hochwitz, J. Slinkman, J. Never, S. Hoffmann, P. Kaszuba and C. Daghljan: J. Appl. Phys. **77** (1995) 1888.
- 13) L. Ley, J. Ristein, J. Schäfer and S. Miyazaki: J. Vac. Sci. Technol. **B14** (1996) 3008.
- 14) W. Graf, K. Leihkamm, M. Wolf, J. Ristein and L. Ley: Phys. Rev. B **53-8** (1996) 4522.
- 15) S. Jin and L. Ley: Phys. Rev. B **44-3** (1991) 1066.
- 16) K. Winer, I. Hirabayashi and L. Ley: Phys. Rev. B **38-11** (1988) 7680.
- 17) T. Yoshida, H. Hasegawa and T. Sakai: Jpn. J. Appl. Phys. **38** (1999) 2349.
- 18) H. Takahashi, T. Yoshida, M. Mutih, T. Sakai and H. Hasegawa: Solid-State Electron. **43-8** (1999) 1561.
- 19) G. S. Higashi, Y. J. Chabal, G. W. Trucks and K. Raghavachari: Appl. Phys. Lett.

56 (1990) 656.

20) Y. Morita and H. Tokumoto: Appl. Phys. Lett. **67** (1995) 2654.

21) F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff and G. Hollinger: Phys. Rev. B **38** (1988) 6084.

22) C. J. Karlsson, F. Owman, E. Landemark, Y. C. Chao, P. Martensson and R. I. G. Uhrberg: Phys. Rev. Lett. **27** (1994) 4145.

23) K. Yamamoto and M. Hasegawa: J. Vac. Sci. Technol. **B12** (1994) 2493.

24) C. H. Bjorkman, J. L. Alay, H. Nishimura, M. Fukuda, T. Yamazaki and M. Hirose: Appl. Phys. Lett. **67** (1995) 2049.

25) Y. Morita and H. Tokumoto: J. Surf. Sci. Soc. Jpn. **20** (1999) 680.

26) T. Yoshida and H. Hasegawa: Jpn. J. Appl. Phys. **39** (2000) 4504.

27) T. Yoshida and H. Hasegawa: Appl. Surf. Sci. (2001) in press.

28) G. J. Pietsch, U. Kohler and M. Henzler: J. Vac. Sci. Technol. **B12** (1994) 78.

29) H. Sakaue, Y. Katsuda, S. Konagata, S. Shingubara and T. Takahagi: Jpn. J. Appl. Phys. **35** (1996) 1010.

30) R. E. Stahlbush: in The Physics and Chemistry of SiO₂ and the Si-SiO₂ Interface 3, H. Z. Massoud, E. H. Poindexter and C. R. Helms, Editors, Proc. **96-1** (1996) 525.

Chapter 5 Passivation of Silicon Surfaces by Ultrathin-Insulating Films

5.1 Introduction

The understanding and control of ultrathin oxide/Si interfaces on an atomic scale will become increasingly important in the future for the continued down-scaling of Si CMOS ULSIs, as well as for the successful development of Si-based quantum device technologies such as the single-electron transistor. However, in spite of recent advances in surface science techniques for characterization of surface nanostructures, such as x-ray photoelectron spectroscopy (XPS)¹⁾, scanning tunneling microscopy (STM)/atomic force microscopy (AFM)^{2,3)}, grazing angle x-ray diffraction (XRD)⁴⁾, Fourier transform infrared-absorption spectroscopy (FTIR)^{5,6)}, etc, no well-established method for characterization of electronic properties of ultrathin-oxide/Si interfaces has been developed.

Some reports^{7,8)} to overcome this difficulty, showed the capability of the combine use of the contactless C-V method and the photoluminescence surface state spectroscopy (PLS³) method to the hydrogen terminated Si(111) surface and surfaces covered with ultrathin low-temperature- (LT-) grown oxide. It was shown that combined use of these two methods is extremely useful in characterizing electronic properties of ultrathin insulator-covered surfaces. It was also shown³⁾ the difficulties to realize ideal ultrathin insulator-covered surfaces free of Fermi-level pinning by the known LT oxidation processes.

However, nitrided oxides and oxynitrides are currently under intensive study for use as gate dielectrics⁹⁻¹¹⁾ due to their superior electrical properties, such as high resistance to hot-carrier degradation and boron diffusion. Furthermore, recent experiments on silicon oxides grown in N₂O have shown that the incorporation of

nitrogen atoms decreases interface state generation.^{12,13)}

In this chapter, further characterization of the electronic properties of various LT-grown ultrathin insulator/Si (111) interfaces were made, using the contactless *C-V* and PLS³ methods in order to realize pinning-free high-quality interfaces. XPS measurements were also made. Ultrathin oxide and oxynitride films were formed using various LT processes¹⁴⁾, paying particular attention to the use of nitrogen-related plasmas.^{15,16)}

Although many oxynitridation processes have been reported, the simplest and most manufacturable one is the direct oxynitridation of Si in N₂O. Among these, the plasma process makes it possible to nitridize or oxynitridize Si surfaces at low temperatures. Thus to study the role of nitrogen atoms in the Si/SiO₂ interface layer, and to obtain a new LT oxynitridation process to produce thin dielectrics with high quality, two types of nitridation and oxynitridation processes were applied in this study. One was N₂-plasma exposure after LT thermal oxidation, and the other was the direct oxynitridation process in which the initial Si surface was exposed to N₂O plasma.

Hydrogen termination was used as the initial surface treatment prior to oxidation, in order to take full advantage of its well-defined flat and highly reproducible atomic structure. As described in chapter 4, well-defined hydrogen terminated surface can be obtained by (111)-oriented surface using NH₄F-based chemical solutions. However, there is no well-established treatment method, i.e. native-oxide-free, atomically flat and clean and stable in the air, for (100)-oriented surface in spite of its usefulness for today's manufacturing. To overcome this problem, in the later part of this chapter, H₂ plasma cleaning process¹⁷⁾ was tried to realize oxide-free well-defined hydrogen terminated (100) surface.

5.2 Formation of ultrathin-insulating films on Si surfaces

In the present study, the hydrogen terminated surface was used as an initial

surface for formation of ultrathin-insulating films on Si surfaces. The hydrogen terminated surface is very attractive for understanding and control of ultrathin insulator films on an atomic scale because of its clean and native-oxide-free nature and its good reproducibility. However, it is not yet clear whether this surface is the most suitable for realizing well-controlled ultrathin insulator/Si interfaces. Thus, further investigation of the effects of process conditions, including surface treatments, on the interface properties is necessary.

The wafers used in this study were n-type silicon (111) with the carrier concentration of $2-3 \times 10^{15} \text{ cm}^{-3}$. The following surfaces^{8,14)} were prepared and characterized:

- (1) chemical oxidized surfaces;
- (2) low-temperature thermally oxidized surface in a vacuum chamber
- (3) nitridized surface which had been covered with low-temperature thermal oxide by (2);
- (4) directly oxynitridized surfaces.

These ultrathin-oxide or oxynitride films were formed on hydrogen terminated surfaces. Details are summarized in **Fig. 5-1** and written as follows.

Chemical oxidation of the hydrogen terminated surfaces was done following the recent work by Ogawa and Hattori, i.e., one immersed into a hot HNO_3 solution (60°C) for 5 min, and the other into a solution of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2=4:1$ for 10 min.

LT thermal oxidation was performed on the hydrogen terminated surface at 400°C for 30 min in dry O_2 at a pressure of 1 Torr in an UHV chamber (base pressure was less than 10^{-9} Torr).

In order to improve the electronic property of the thermally oxidized surfaces, electron cyclotron resonance (ECR) plasma treatments were applied. N_2 -plasma nitridation was performed by exposing the low-temperature thermally oxidized surface to N_2 plasma with the gas flow rate of 5 sccm (gas pressure was 10^{-3} Torr) in an UHV chamber at 400°C for 30 min. The microwave power was 100 W. Diagrams of the UHV chamber for ECR-plasma processes and the gas supplying/control system

Condition for ultrathin-oxide or oxynitride films on Si

(1) Chemically oxidation

- Hydrogen termination → HNO_3 (60%) 1.1 nm
60 °C, 5 min.

- Hydrogen termination → $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 4:1$ 1.0 nm
85 °C, 10 min.

(2) Low-temperature thermally oxidation

- Hydrogen termination → dry O_2 (1 Torr) 0.8 nm
400 °C, 30 min.
in UHV chamber

(3) Nitridation of low-temperature thermal oxide covered surface

- Low-temperature thermally oxidation
(same as (2)) → - ECR- N_2 plasma exposure 4 nm
(pressure : 10^{-4} Torr
substrate temperature : 400 °C
exposing time : 30 min.
microwave power : 100 W)

(4) Direct oxynitridation

- Hydrogen termination → - ECR- N_2O plasma exposure 4 nm
(pressure : 10^{-4} Torr
substrate temperature : 400 °C
exposing time : 30 min.
microwave power : 100 W)

Fig. 5-1 Summarize of conditions for ultrathin-insulating film formation used in this study.

used in this study is schematically shown in **Fig. 5-2 (a)** and **(b)**, respectively.

Furthermore, by exposing the hydrogen terminated surface to the ECR-N₂O plasma at a microwave power of 100 W in an UHV chamber, direct oxynitridation of the silicon surface was attempted. The substrate temperature and exposing time were 400°C and 30min, respectively. And the flow rate of N₂O gas was 5 sccm (gas pressure was 10⁻³ Torr).

Thicknesses of above four type of ultrathin-oxide and oxynitride films are also summarized in **Fig. 5-1**, which were calculated using the integral intensities of XPS Si2p spectra described in Sec. 5.3.2.

5.3 Properties of ultrathin-insulator-covered Si surfaces

5.3.1 UHV contactless *C-V* characterizations

Figures 5-3 (a) and **(b)** show the contactless *C-V* curves after two-types of chemical oxidation processes of hydrogen terminated surfaces. As seen in **Fig. 5-3**, the *C-V* behaviors are completely different from that of the hydrogen terminated surface shown in chapter 4. An extremely limited capacitance variations are seen at a lower capacitance level to theoretical one. These behaviors indicate presence of a high density of interface states which cause a strong Fermi level pinning on chemically oxidized surfaces. The capacitance analysis indicates that the pinning position is at about 0.30-0.40 eV from the valence band edge. It should be noted that the observed energy position is close to the hybrid-orbital charge neutrality level, $E_{HO}^{18)}$, of 0.32 eV, or to the Tersoff's midgap energy level¹⁹⁾ of 0.36 eV for Si.

Figures 5-4 (a)-(c) show the contactless *C-V* curves after three types of thermal oxidation and oxynitridation processes. As shown in **Fig. 5-4 (a)**, the LT thermally oxidized surface exhibited very limited *C-V* variations at a low capacitance

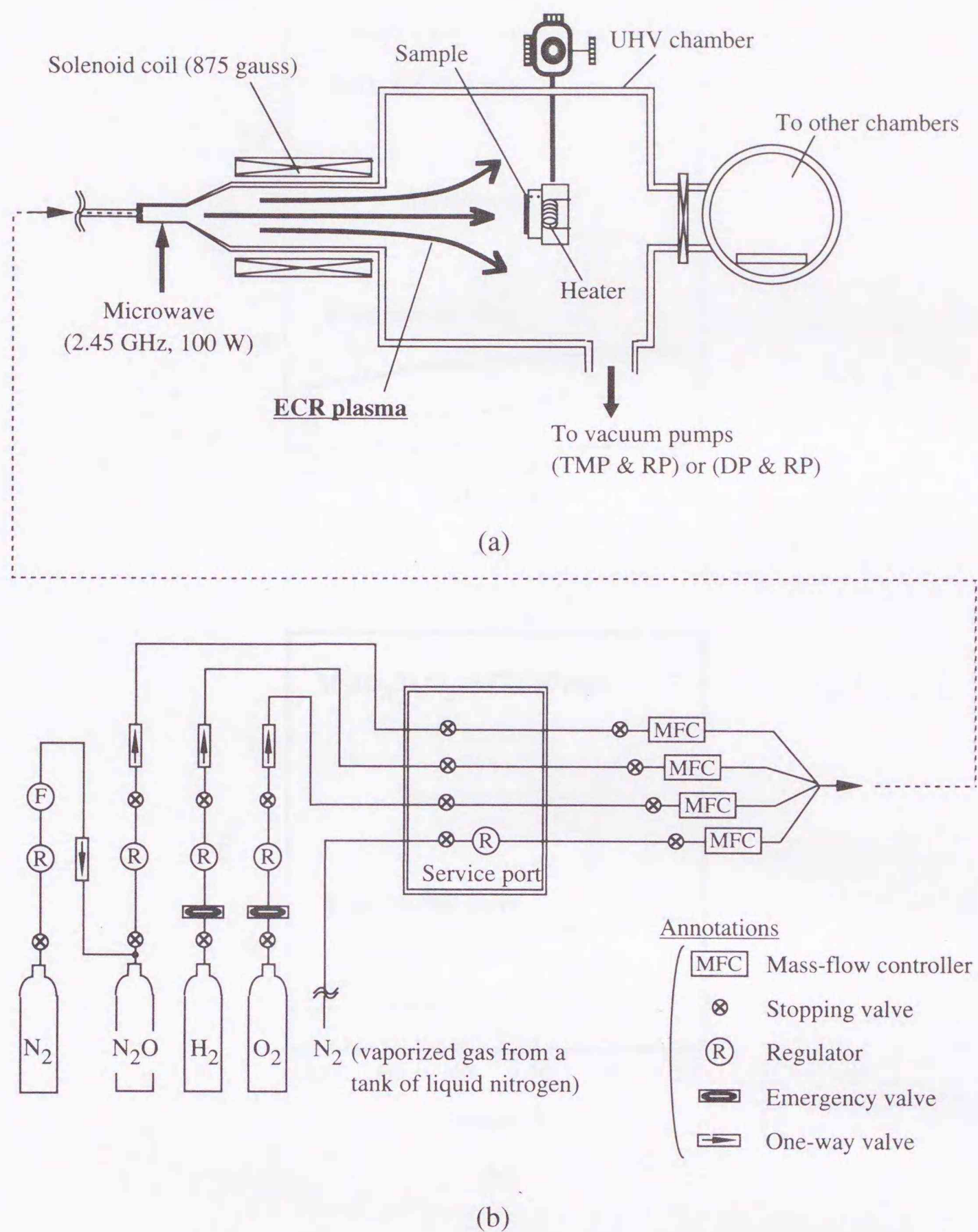


Fig. 5-2 Diagrams of (a) UHV chamber for ECR-plasma process and (b) the gas supplying/control system used in this study.

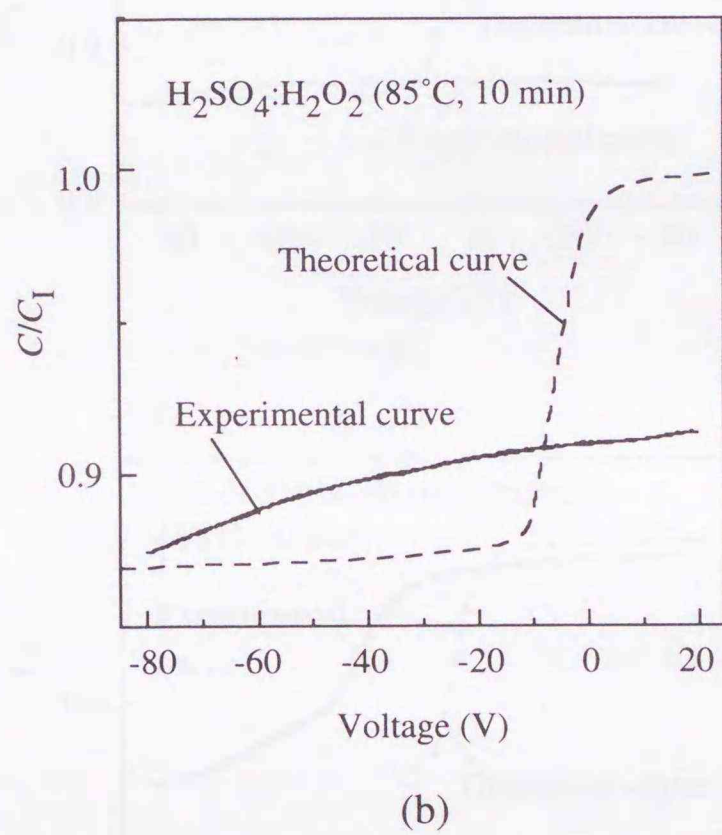
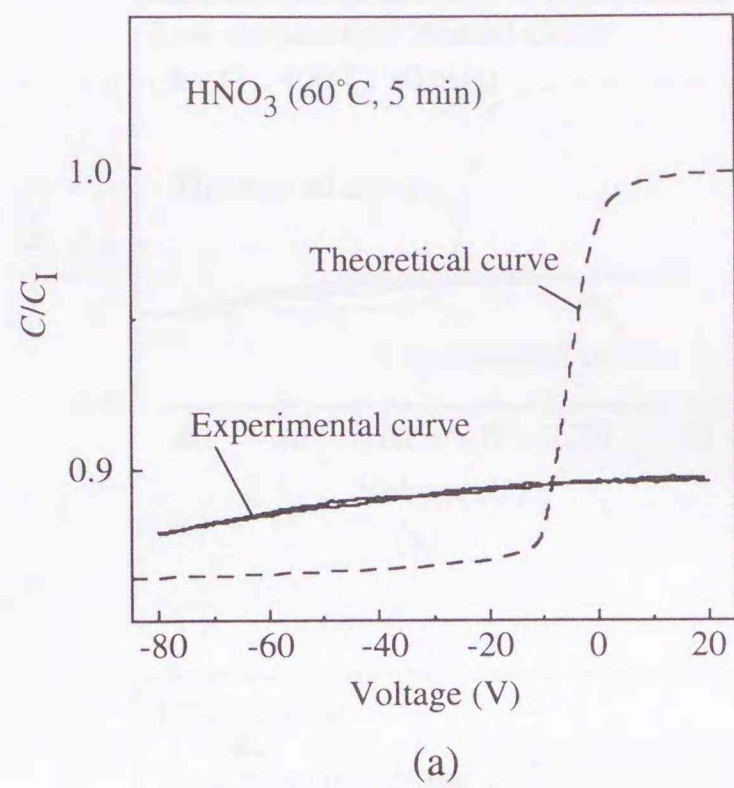
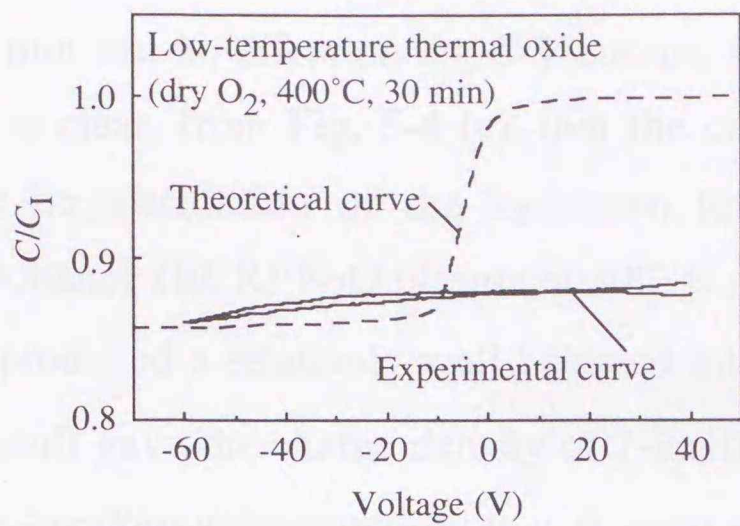
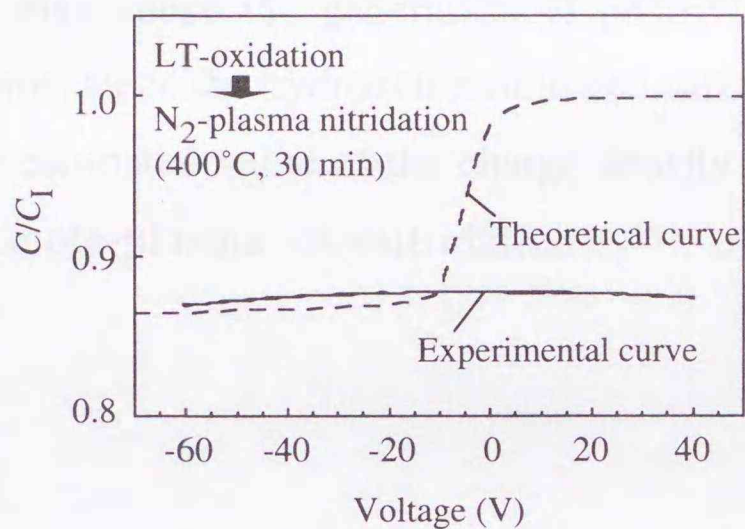


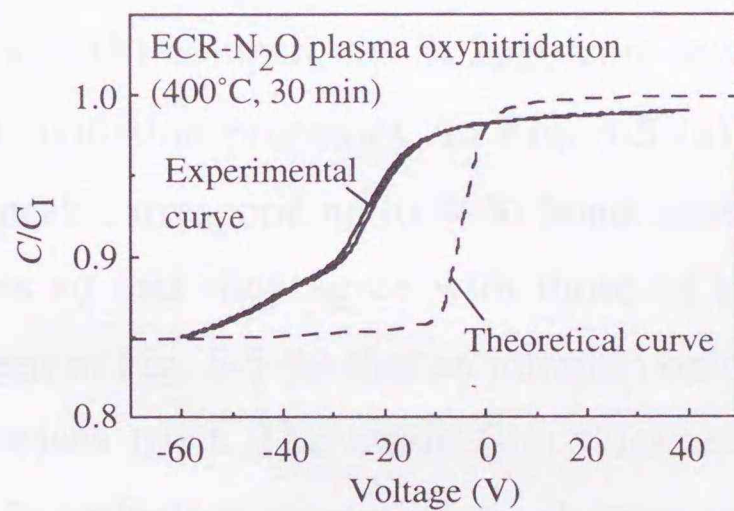
Fig. 5-3 Contactless C - V curves after chemical oxidation.



(a)



(b)



(c)

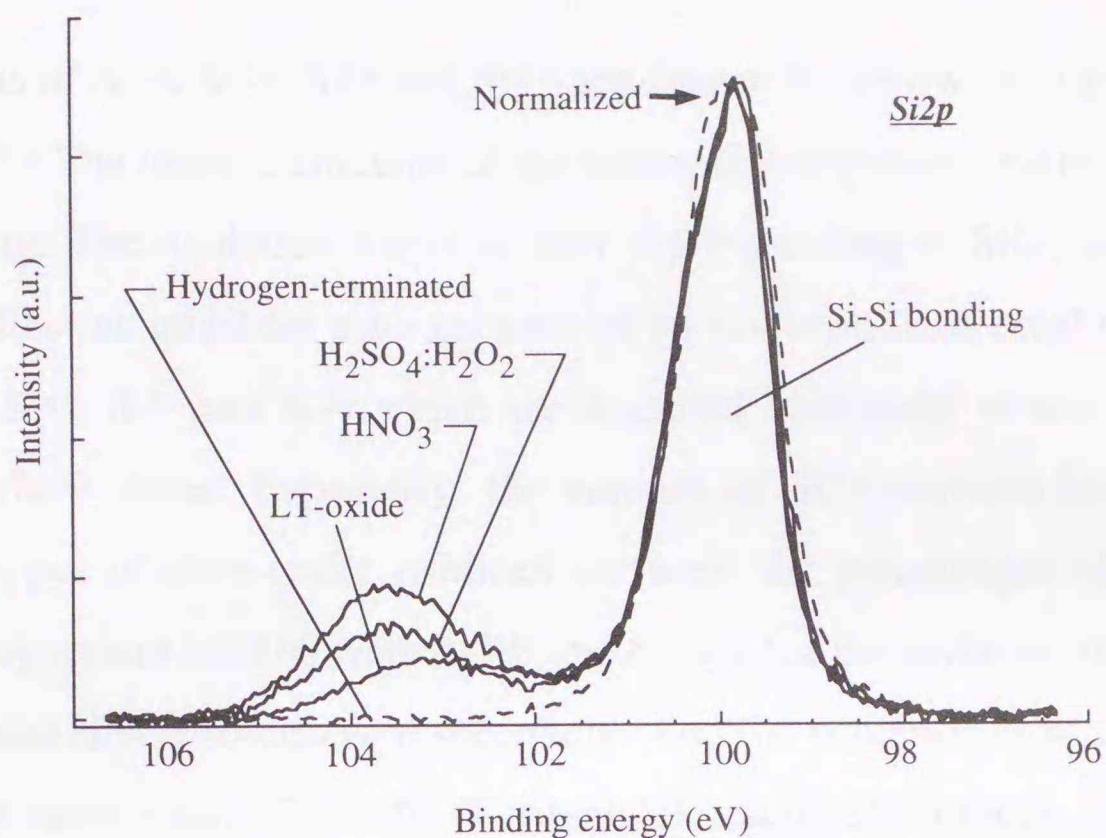
Fig. 5-4 Contactless C - V curves taken on (a) a low-temperature thermally oxidized surface, (b) subsequent N₂-plasma exposed surface and (c) direct ECR-N₂O plasma oxynitridized surface.

level, indicating the presence of a high density of interface states. N_2 -plasma treatment at 400°C for 30 min had no effect on the C - V curves, as shown in **Fig. 5-4 (b)**. On the other hand, it is clear, from **Fig. 5-4 (c)**, that the capacitance variation was greatly enhanced by oxynitridation of the hydrogen terminated surface using electron-cyclotron-resonance (ECR)- N_2O plasma at 400°C , indicating that the ECR- N_2O plasma process produced a relatively well-behaved interface. An estimation of the flat-band voltage shift gave the charge density of $2\text{-}3 \times 10^{11} \text{ cm}^{-2}$ in the oxynitride film. Lucovsky and co-workers^{16,20)} proposed that H-atom migration-related defects may lead to the creation of positively charged centers in ultrathin oxide or oxynitride film. Similar centers may cause the generation of positive charges in the present ultrathin oxynitride films, since the hydrogen terminated surface was used as an initial surface. However, the estimated value of the charge density is as low as those in the films formed by remote-plasma oxynitridation^{16,29)} or rapid-thermal-anneal oxynitridation⁹⁾.

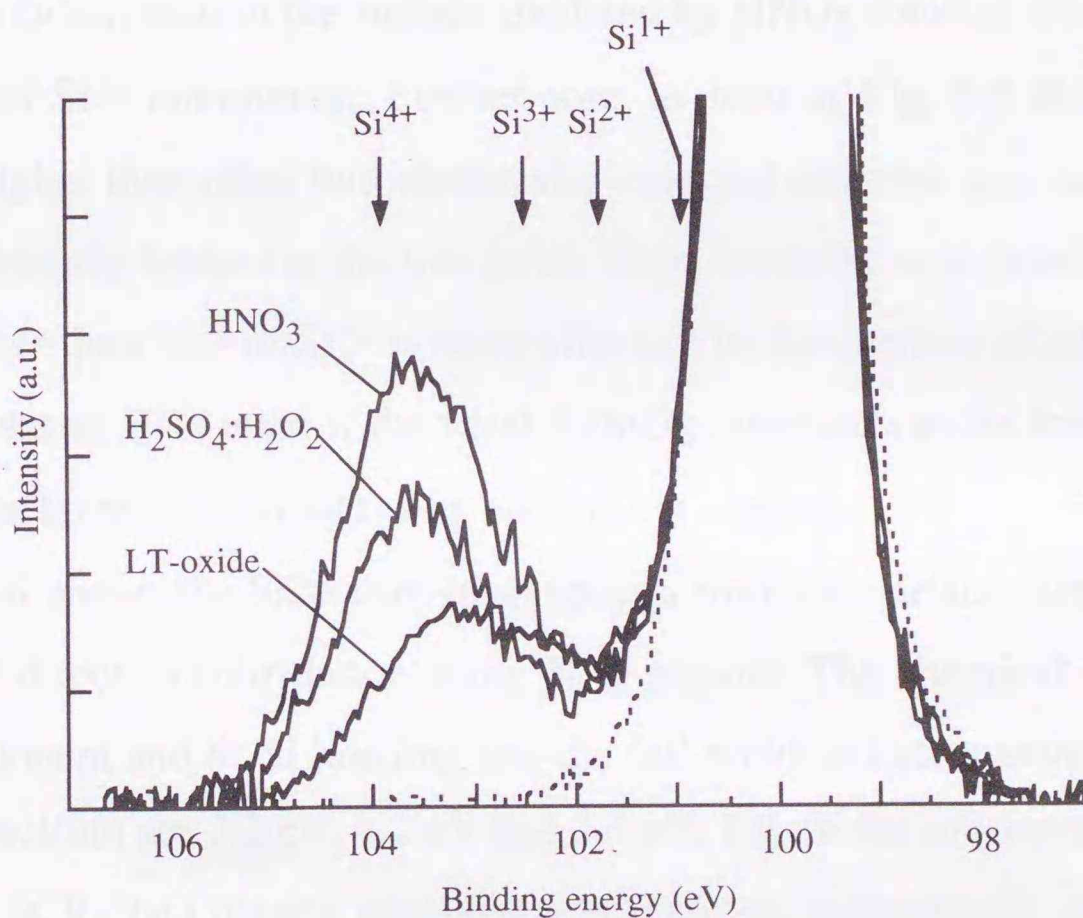
5. 3. 2 XPS analyses

Figures 5-5 (a) and (b) compare the Si $2p_{3/2}$ core-level spectra obtained after chemical and thermal oxidation processes. In **Fig. 5-5 (a)**, the peak position and height of the main Si peak corresponding to Si-Si bond were shifted and adjusted for each oxidation process so that they agree with those of the hydrogen terminated surface. It is clearly seen in **Fig. 5-5 (a)** that an ultrathin oxide was formed after each of the oxidation processes tried. The oxide film thickness can be calculated by analyzing these Si2p photoelectron spectra, if the electron escape depth in Si and Si-oxide are 2.6 nm and 3.4 nm, respectively. The estimated thickness values are 1.1 nm, 1.0 nm and 0.8 nm for chemically oxidized surfaces using HNO_3 solution, $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$ solution and thermally oxidized surface at 400°C , respectively (summarized in **Fig. 5-1**). And, these values are in good agreement with those in the literature.

In order to see the intermediate oxidation status more carefully, oxide peaks are shown in a magnified scale in **Fig. 5-5 (b)**. The positions corresponding to the



(a)



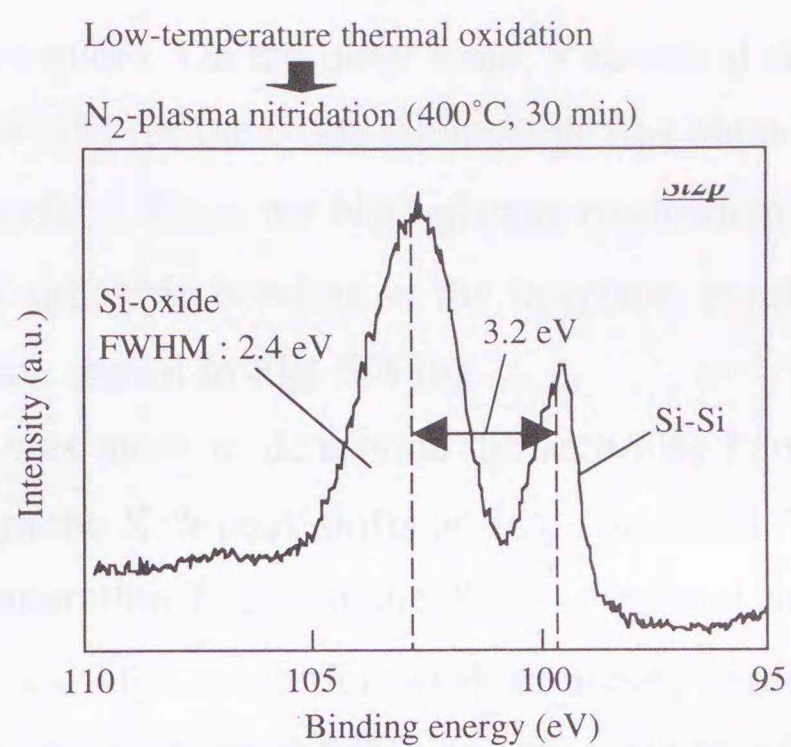
(b)

Fig. 5-5 (a) XPS Si2p spectra of hydrogen terminated and various kinds of ultrathin-oxide covered surfaces. The peak position and height of the main Si peak corresponding to Si-Si bond were shifted and adjusted for each oxidation process so that they agree with that of the initial hydrogen terminated surface. (b) Spectra are shown in magnified scale.

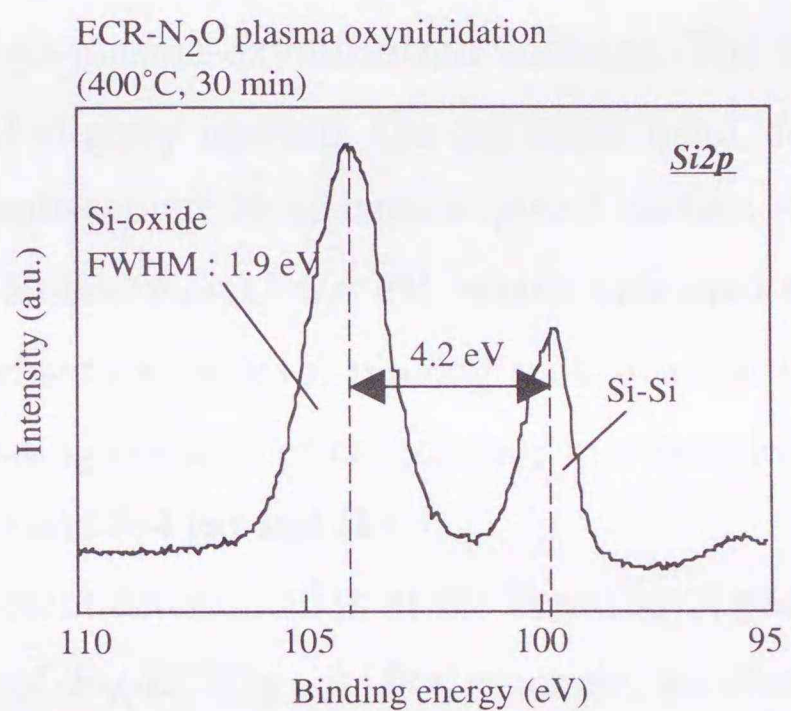
oxidation status of Si^{1+} , Si^{2+} , Si^{3+} and Si^{4+} are shown by arrows using the data by Himpsel *et al.*²¹⁾ The relative amounts of the suboxide components were separated by the curve fitting. The oxidation status of Si^{4+} corresponding to SiO_2 can be recognized not to affect as interface state because of its perfectness of bonding. So, other status such as Si^{1+} , Si^{2+} and Si^{3+} which are so-called "suboxide" is one of thinkable origin of interface states. Especially, the amount of Si^{3+} showed large different between two-types of chemically oxidized surfaces; the percentages of Si^{3+} compared to Si-Si spectrum ($=\text{Si}^{0+}$) were 1-3% and 8-10% for the surfaces oxidized using $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$ and HNO_3 solutions, respectively. And the percentages of Si^{1+} and Si^{2+} showed almost same values for both of chemically oxidized surfaces. In **Fig. 5-3**, a relatively larger capacitance variation can be seen in the surface oxidized by $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$ solution than in the surface oxidized by HNO_3 solution which possesses larger amount of Si^{3+} component. Furthermore, as seen in **Fig. 5-5 (b)**, the ratio of Si^{3+} is much higher than other two chemically oxidized surfaces, and the capacitance variation is extremely limited at the low level. Thus, it can be considered that the Si^{3+} component rather than Si^{1+} or Si^{2+} is more effective to the creation of interface states. Here, we will detect Si^{1+} even if the ideal Si/ SiO_2 interface can be formed, since it needs, at the first layer, to form SiO_2 film on Si (111) surface.

Figure 5-6 shows the Si2p core-level spectra from the surfaces after N_2 -plasma nitridation and direct oxynitridation using N_2O plasma. The chemical shift between the oxide component and Si-Si bonding and the full-width at half-maximum (FWHM) of the oxide spectrum are 3.2 eV, 4.2 eV and 2.4 eV, 1.9 eV for subsequent N_2 plasma nitridized and ECR- N_2O plasma oxynitridized surfaces, respectively. And the oxide thicknesses of both oxynitride layer were calculated to 4 nm each other. The peak position and FWHM of XPS spectra of the LT thermally grown surface was almost the same before and after the N_2 -plasma nitridation, although the peak height of the oxide component increased after the N_2 -plasma nitridation.

For N_2 -plasma-treated surface, as shown in **Fig. 5-6 (a)**, the value of chemical shift of oxide component is much smaller than the known value of 3.9-4.2 eV for the



(a)



(b)

Fig. 5-6 The $\text{Si}2p$ core level spectra from the surfaces after (a) subsequently N_2 -plasma nitridation and (b) direct N_2O -plasma oxynitridation.

SiO₂ bonding. This strongly indicates that there are large amounts of suboxide at the LT thermal oxide/Si interface even after N₂-plasma nitridation, which may cause the high density of interface states. On the other hand, a chemical shift with the value of 4.2 eV and narrower FWHM for the oxide component was obtained at the ECR-N₂O-plasma-oxynitridized surface. Thus, the N₂O-plasma oxynitridation process probably reduces the number of suboxide bonding at the interface, resulting in the enhancement of the *C-V* variation shown in **Fig. 5-4 (c)**.

Then, an attempt was made to determine the zero-bias Fermi level positions of the sample surfaces from the XPS peak shifts of Si2p core-level. To do this, one needs to know the energy separation between the Si2p core-level and the valence-band edge. Himpsel *et al.*²²⁾ did high resolution work on nearly intrinsic Si wafers which gave $E_V - E(\text{Si}2p_{3/2}) = 98.86$ eV. **Figure 5-7** shows the zero-bias Fermi-level positions obtained from the peak positions of the Si2p spectra at the LT-oxidized, N₂-plasma nitridized and ECR-N₂O-plasma-oxynitridized surfaces. The N₂O-plasma process moves the Fermi level slightly upward. On the other hand, for the LT thermally oxidized surface and subsequent N₂-plasma-exposed surface, the Fermi level was found to be pinned at around $E_V + 0.3$ - 0.4 eV, which indicated that the strong band-bending due to the surface Fermi level pinning took place at these surfaces which correspond to the flattening position of capacitance in contactless *C-V* curves shown in **Figs. 5-3 (a) and (b)** and **5-4 (a) and (b)**.

Obviously, the present determination of the Fermi level position depends on the accuracy of the value of $E_V - E(\text{Si}2p_{3/2})$. For example, another group²³⁾ gave $E_V - E(\text{Si}2p_{3/2}) = 98.74$ eV, and this would shift the result shown in **Fig. 5-7** upward 0.12 eV. In order to check the validity of the reference value of $E_V - E(\text{Si}2p_{3/2})$, further attempt was applied to hydrogen terminated surface prepared by BHF/H₂O₂/NH₄F treatment. As mentioned in chapter 4, this type of hydrogen terminated surface possesses a discrete surface state with high density which caused a Fermi level pinning at around 0.65 eV above the valence band edge²⁴⁾. The directly measured Fermi level position by measuring the valence -band spectrum was 0.62 ± 0.05 eV, and this value shows good agreement with the energy position calculated by XPS Si2p_{3/2}

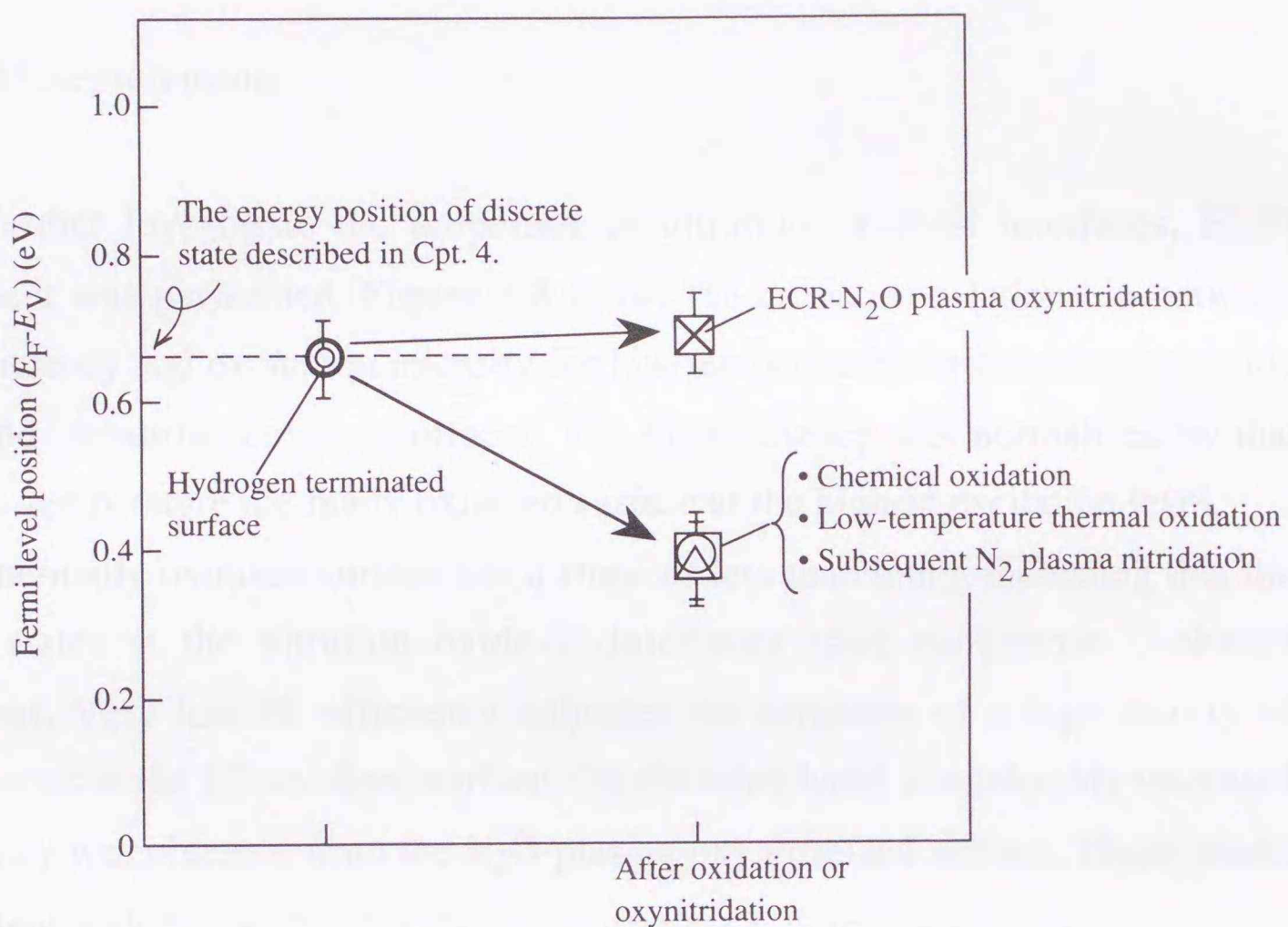


Fig. 5-7 The zero-bias Fermi level positions obtained from the peak positions of the Si2p spectra at various kinds of surfaces.

spectrum using $E_V - E(\text{Si}2p_{3/2}) = 98.86$ eV and the energy position of discrete surface state described in chapter 4. So, the latter case, $E_V - E(\text{Si}2p_{3/2}) = 98.74$ eV, might be wrong.

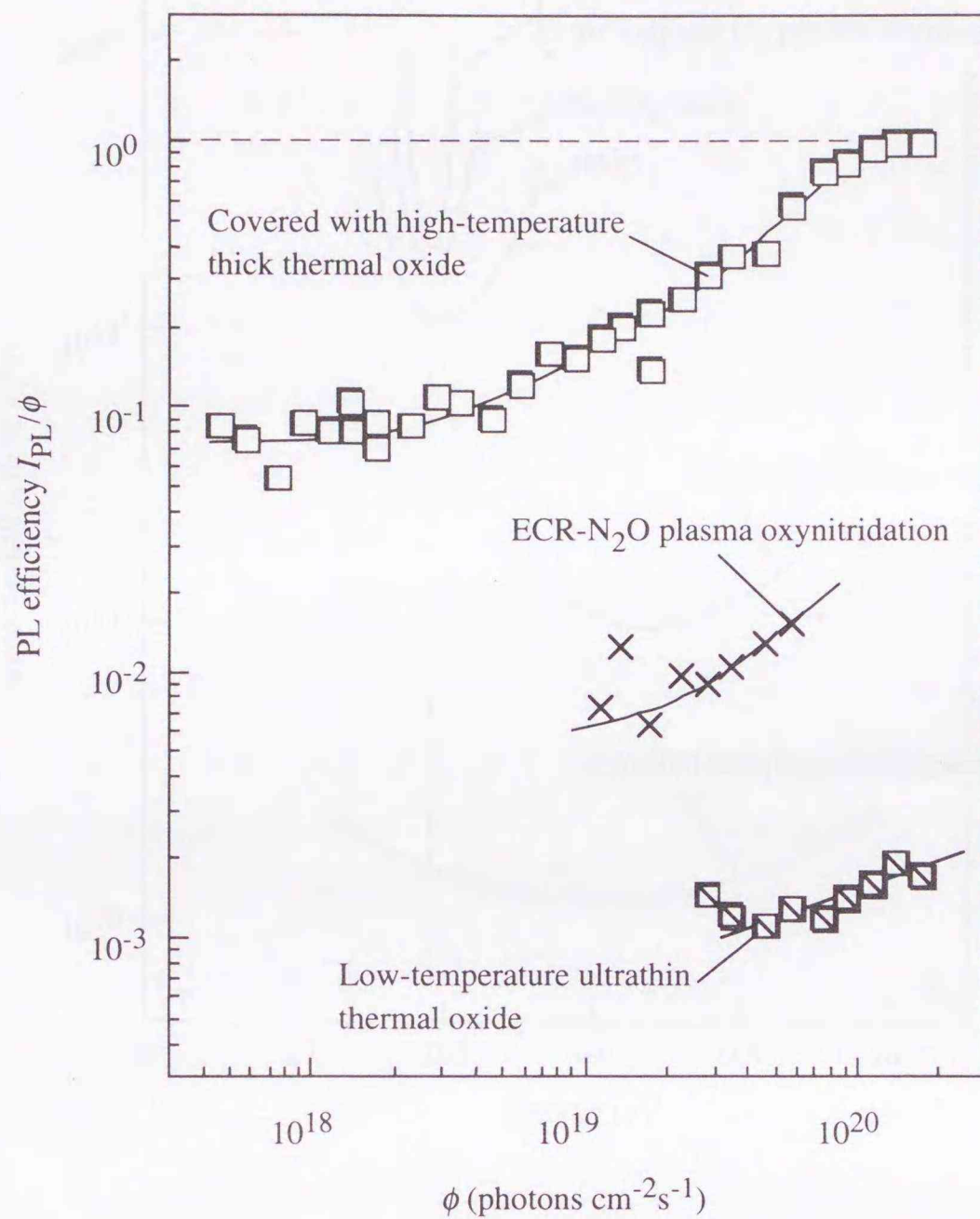
5.3.3 PLS³ measurements

To further investigate the properties of ultrathin oxide-Si interfaces, PLS³ measurement was performed. **Figure 5-8** shows the measured relationship between the PL efficiency and excitation intensity for low-temperature ultrathin thermal oxide covered and oxynitride covered surfaces. The PL efficiency was normalized by that of the high-temperature thermally oxidized surface at the highest excitation level.

LT-thermally oxidized surface has a slope of less than unity, indicating that the interface states at the ultrathin oxide-Si interfaces have continuous U-shaped distributions. Very low PL efficiency indicates the existence of a high density of interface states at the LT-oxidized surface. On the other hand, considerably increased PL efficiency was obtained from the N₂O-plasma-oxynitridized surface. These results are consistent with the results of XPS and contactless *C-V* measurements.

Figure 5-9 shows the interface state distributions determined by combining all of the experimental results of the contactless *C-V*, XPS and PLS³ methods for the various surfaces.

In the case of the LT thermally oxidized surface and the subsequent N₂-plasma-treated surface, all experimental results showed the existence of high-density interface states of the order of 10^{12} cm⁻²eV⁻¹. These states have a continuous and extremely narrow U-shaped distribution, and pin the surface Fermi levels at around 0.3-0.4 eV above the valence band. On the other hand, the surfaces obtained after oxynitridation by ECR-N₂O plasma exhibit a wider U-shaped surface state density distribution with a minimum value of about 1×10^{11} cm⁻²eV⁻¹. Such reduction of interface states enhanced the *C-V* variation and PL efficiency.



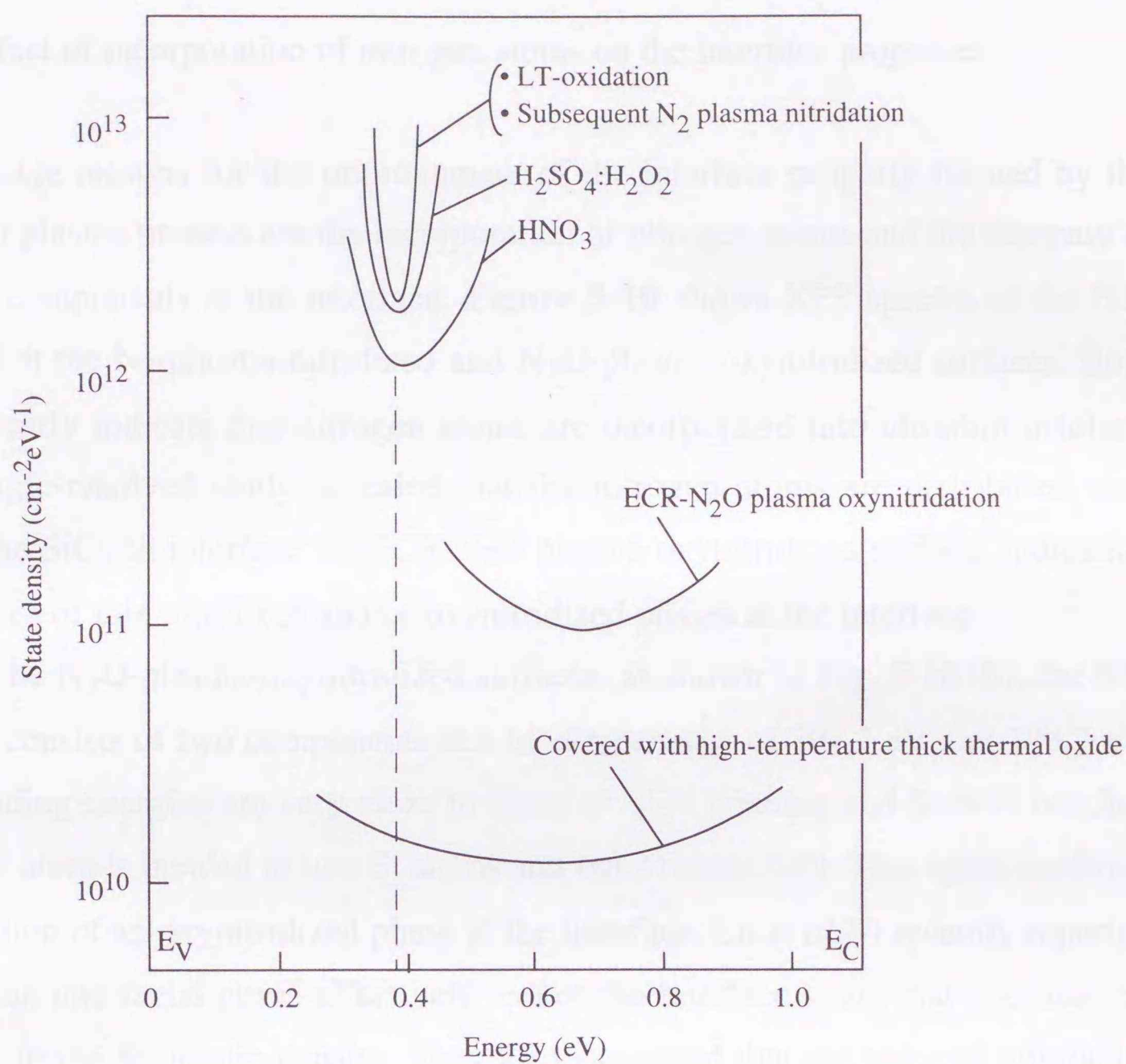


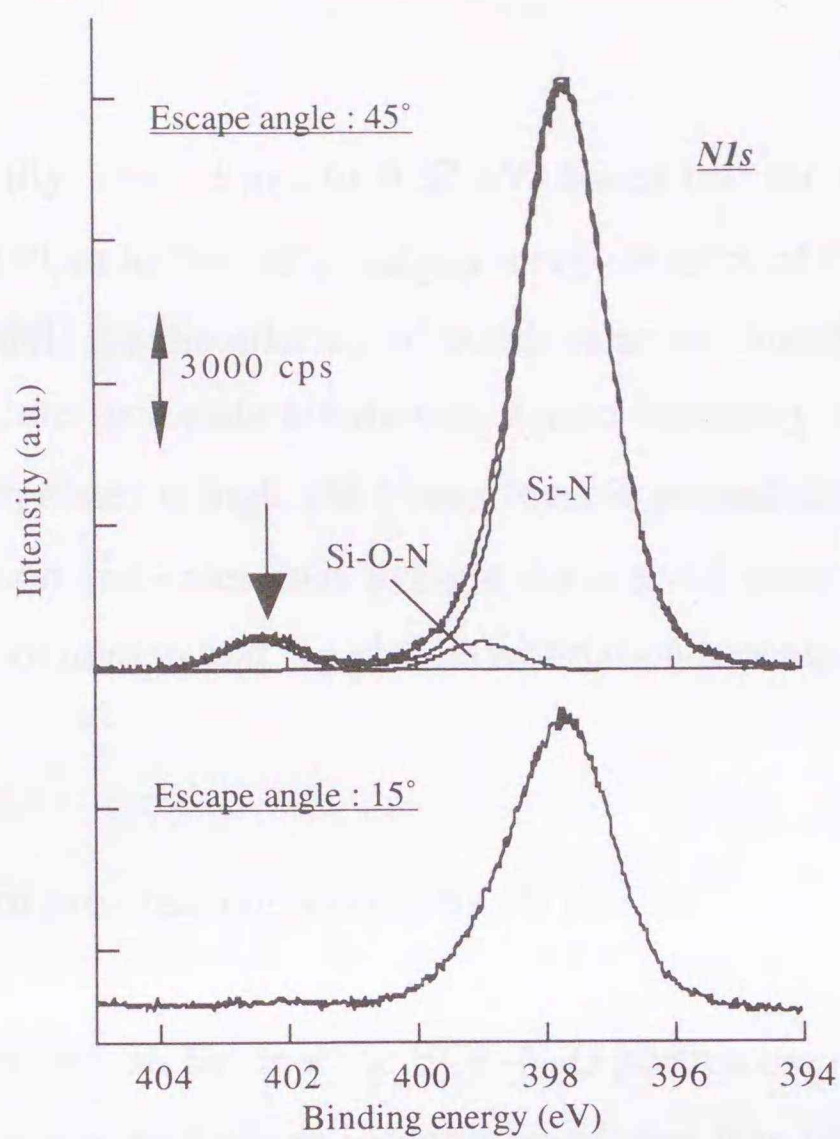
Fig. 5-9 Schematic model of interface state density distributions estimated from the results of contactless C - V , XPS and PLS³ measurements for various Si surfaces.

5. 3. 4 Effect of incorporation of nitrogen atoms on the interface properties

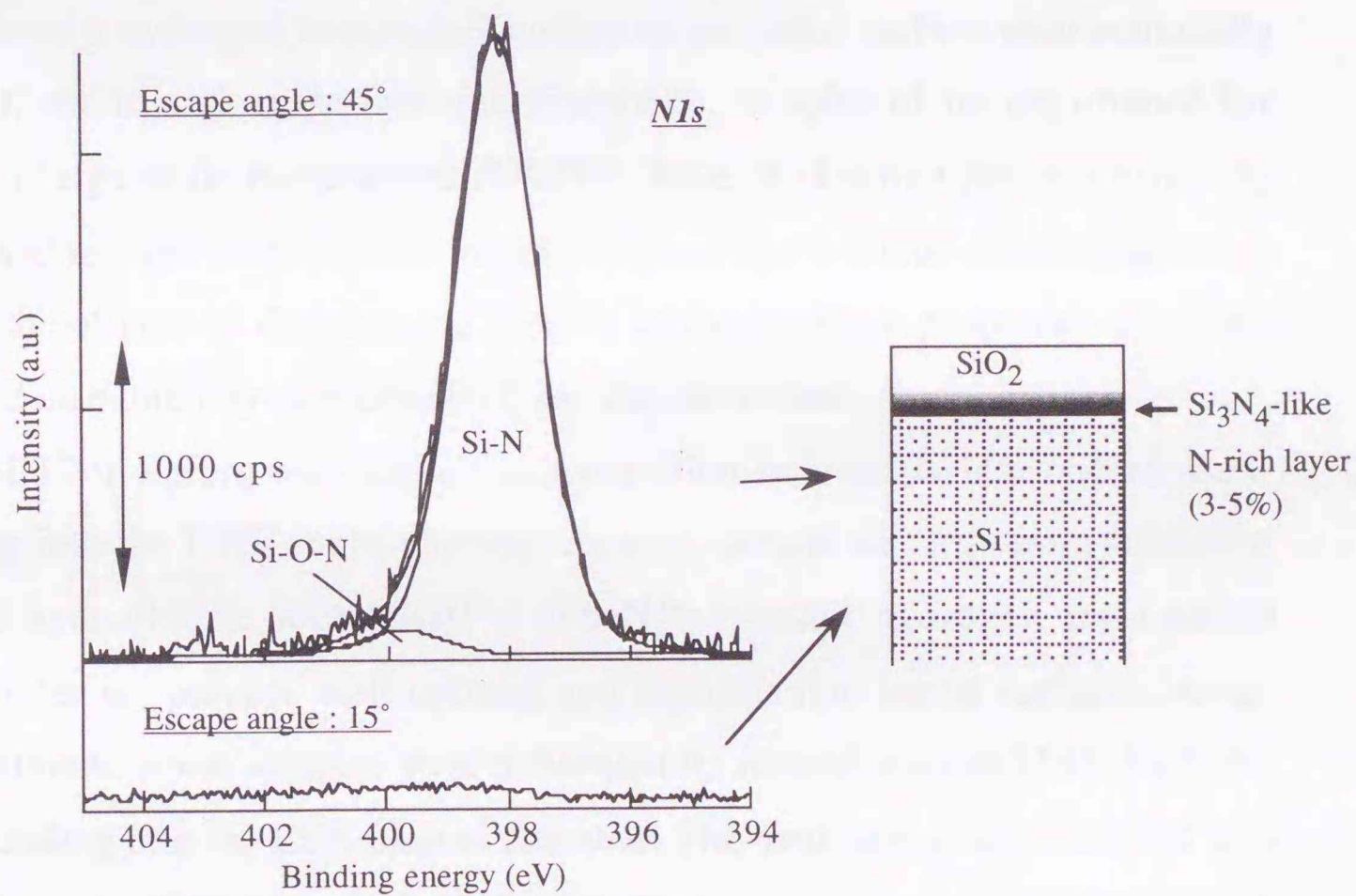
Possible reasons for the improvement of the interface property formed by the ECR-N₂O plasma process are the incorporation of nitrogen atoms and the decrease of suboxide components at the interface. **Figure 5-10** shows XPS spectra of the N1s core level at the N₂-plasma-nitridized and N₂O-plasma-oxynitridized surfaces. Both spectra clearly indicate that nitrogen atoms are incorporated into ultrathin insulator films. Angle-resolved study revealed that the nitrogen atoms are distributed very close to the SiO₂/Si interface for ECR-N₂O plasma oxynitridized surface, indicating the presence of thin nitridized and/or oxynitridized phases at the interface.

For the N₂O-plasma-oxynitridized surfaces, as shown in **Fig. 5-10 (b)**, the N1s spectrum consists of two components at a binding energy of 398.2 eV and 399.7 eV. These binding energies are very close to those of Si-N bonding and Si-N-O bonding where a N atom is bonded to two Si atoms and one O atom^{25,26}). This again confirms the formation of an oxynitridized phase at the interface. Lu *et al.*²⁷) recently reported that such an interfacial phase effectively reduce the interface strain that is caused by mismatch in the Si atomic density. They also suggested that the reduced interfacial strain causes the reduction of suboxide components. Thus, such effects may take place at the interface formed by the present ECR N₂O-plasma process.

At the LT thermally oxidized surface after N₂-plasma nitridation, as shown in **Fig. 5-10 (b)**, a distinct peak at a binding energy of around 402.5 eV was seen in the N1s spectrum. The origin of this peak is not yet clear, but there exists an additional bonding state of the N atom at the N₂-plasma-nitridized oxide/Si interface. Such a complicated chemical status is likely to change the chemical environment of the Si and O atoms, leaving dangling bonds and a disordered interface. This situation seems to cause the creation of a large amount of suboxide components, as seen in Fig. 8(a). In fact, the surface Fermi levels on the N₂-plasma-nitridized surfaces were pinned at 0.35-0.4 eV above the valence band. This value is very close to the hybrid orbital



(a) LT-oxidation z N₂ plasma nitridation



(b) ECR-N₂O plasma oxynitridation

Fig. 5-10 The XPS N1s spectra for surfaces after (a) subsequent N₂ plasma nitridation and (b) ECR-N₂O plasma oxynitridation with the escape angle of 45° and 15°. One of thinkable structural models of ECR-N₂O oxynitridized sample is schematically shown in (b).

charge neutrality level, E_{HO} , of 0.32 eV, based on the disorder-induced gap state (DIGS) model¹⁸⁾, or to Tersoff's midgap energy level¹⁹⁾ of 0.36 eV for Si. According to the DIGS model, the disordering of bonds near the interface produces a donor- and acceptor-like interface state continuum whose boundary is given by E_{HO} . When the density of such states is high, the Fermi level is pinned at E_{HO} . Thus, the Fermi-level pinning position indicates that a bond-disordered interface layer may be formed during the LT oxidation and N_2 -plasma nitridation process.

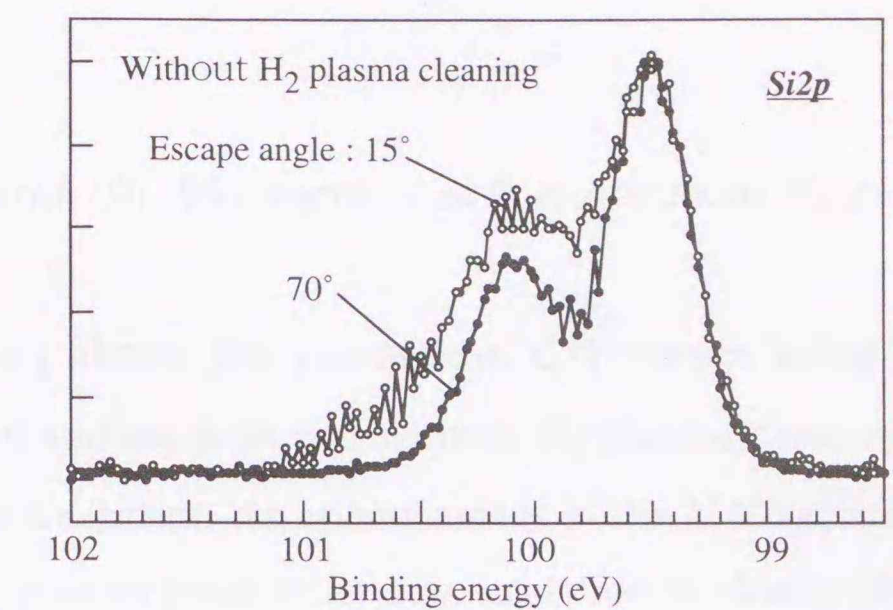
5. 3. 5 Effect of pre-cleaning process by H_2 plasma

It is described, so far, that the ECR- N_2O plasma oxynitridation process is one of promising processes to form an ultrathin insulating film on well-determined hydrogen terminated Si(111) surface. However, for (100) surface, there is no well-established technique to form a hydrogen terminated surface as an initial surface with atomically clean and flat, stable and oxide-free characteristics, in spite of its importance for industrial ultra-large-scale-integrations (ULSIs). Here, a cleaning process using H_2 plasma was tried to form well defined initial (100) surface without oxide component. Furthermore, the effects of the cleaning process to the interface properties of subsequently formed ultrathin oxynitride/Si(100) are also described.

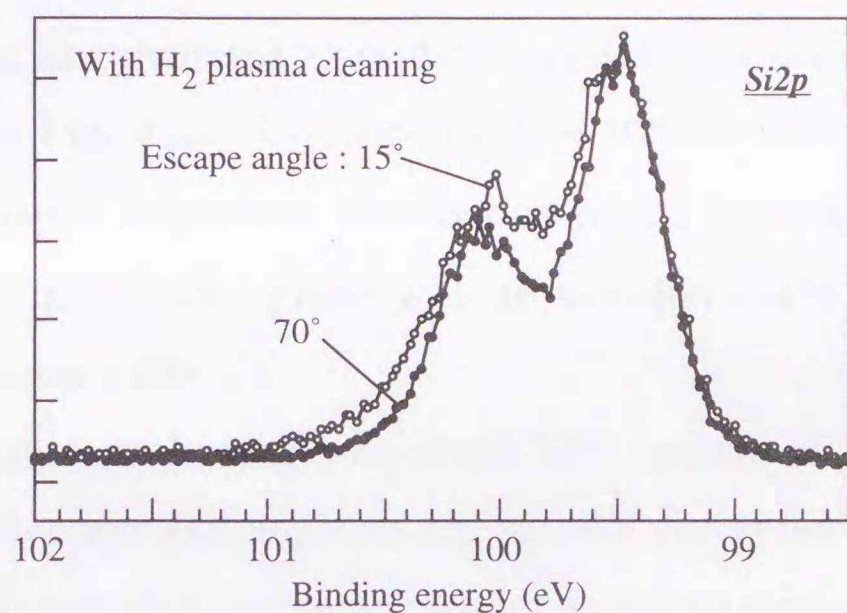
n-type Si(100) wafers with carrier concentration of $4\text{--}6 \times 10^{14} \text{cm}^{-3}$ were used. Before loading into the UHV multi-chamber-system, sample surfaces were subjected to a buffered-hydrofluoric-acid- (BHF-) and NH_4F -based hydrogen termination treatment in order to prepare well-defined and reproducible initial surfaces. As an additional treatment, some samples were subsequently treated with an UHV ECR- H_2 plasma after loading into the ECR plasma chamber. The treatment was made for 1 min at 200 °C with a gas flow rate of 10 sccm at a microwave power of 100 W ($f=2.45$ GHz). Then oxynitridation was carried out at 400 °C for 5 min by exposing the surface directly to the ECR- N_2O plasma with the microwave power of 100 W with a gas flow rate of 5 sccm (gas pressure was about 10^{-4} Torr).

Comparison of initial surfaces with and without H₂ plasma cleaning process

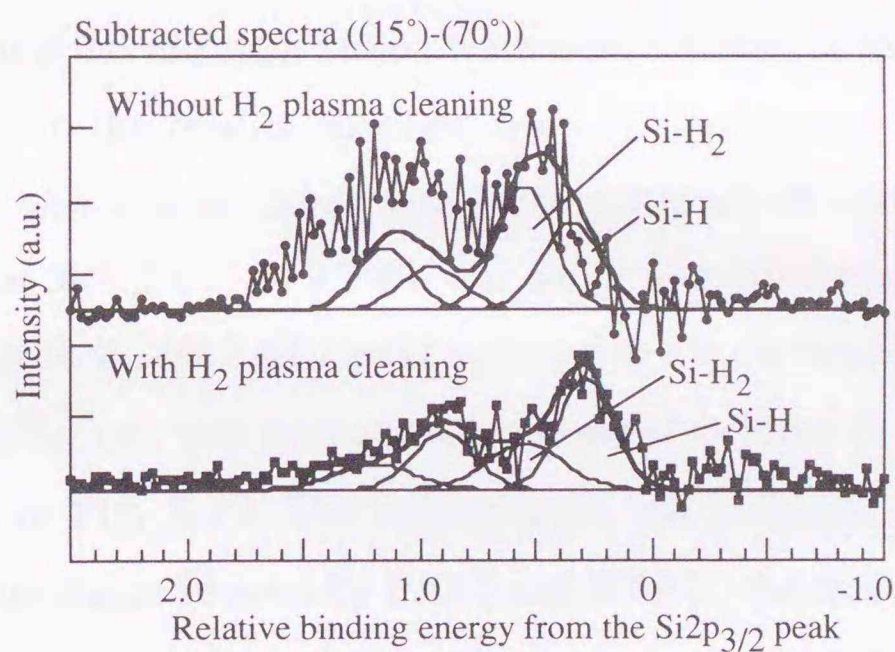
Figure 5-11 (a) and (b) show high-resolution Si2p core-level spectra taken at two escape angles of 70° and 15° for surfaces with and without H₂ plasma treatment, respectively. For both cases, the spectra with a escape angle of 70° could be successfully deconvoluted into the Si2p_{1/2} and Si2p_{3/2} peaks respectively, to be equal to 0.5 and peak energy separation of 0.6 eV. This indicated that spectra with a escape angle of 70° include almost all of the bulk component. As compared to this, it is clear that additional surface components appear in the spectra with a escape angle of 15°. **Figure 5-11 (c)** compares the spectra obtained from the actual subtraction of the intensities of the x-ray photoelectrons from the 15° spectra of the 70° spectra. The abscissa indicates the energy separation from Si2p_{3/2} peak position of the 70° spectra. For the surface with the H₂ plasma treatment, the subtracted spectra also had two peaks which could be well fitted by the Si-H (chemical shift : 0.3 eV) and the Si-H₂ (chemical shift : 0.5 eV) related bonds²⁸⁻³⁰) considering peak ratio of 0.5 and energy separation of about 0.6 eV. This indicates that the surface exposed to ECR-H₂ plasma was hydrided. Bjorkman *et al.*³⁰) and Yamamoto and Hasegawa²⁹) reported that both the mono-hydride and di-hydride components exist at the Si(100) surfaces treated in HF solution and by atomic hydrogen in the UHV chamber. As seen from the upper spectrum in **Fig. 5-11 (c)**, the surface without H₂ plasma treatment seems to also have H-related components. However, it is clearly noticeable that both the intensity and FWHM of the higher-energy peak was remarkably higher than the theoretical ones. This obviously indicated that on this surface, an appreciable amount of native oxide components remained after the BHF- and NH₄F-based wet chemical treatment. Judging from the peak position relative to the Si2p_{3/2} peak, the additional peak seems to originate from Si¹⁺ suboxide component. In fact, Aiba *et al.*³¹) reported that the Si¹⁺ is the dominant suboxide at the Si(100) surface after BHF treatment and a subsequent low-temperature (300°C) oxidation in dry O₂. These components could thus be removed on an additional exposure of the Si(100) surface to ECR-H₂ plasma.



(a)



(b)



(c)

Fig. 5-11 High resolution Si2p core-level XPS spectra for surfaces (a) with and (b) without H₂ plasma cleaning process with escape angle of 15° and 70°. (c) Spectra obtained by subtracting the intensities of the photoelectrons from the 15° spectrum to the 70° spectrum in (a) and (b).

Properties of oxynitride/Si(100) interface with and without H₂ plasma cleaning process

Figure 5-12 (a) shows the contactless *C-V* curves taken on the ECR-N₂O plasma oxynitridized surface with and without H₂ plasma cleaning process as a part of our initial surface treatment. An enhancement in the *C-V* variation on treatment of the surface with H₂ plasma prior to its oxynitridation is clearly observed, indicating the formation of a relatively well-behaved interface. The distributions in the density of the interface states, as calculated from the measured *C-V* curves using Terman's method, are shown in **Fig. 5-12 (b)**. The interface treated with H₂ plasma gave a wider and lower U-shaped continuous distribution with a minimum value of $1 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$, even in the as-prepared phase with an ultrathin oxide thickness (2.8 nm) formed at low-temperature (400 °C).

Figure 5-13 compares the angle-resolved XPS spectra of the N1s core-level taken with the photoelectron exit angle of 15° and 45° for either surfaces, i.e., with and without the H₂ plasma cleaning process prior to the oxynitridation process. For both surfaces, it was found that the concentration of the nitrogen atom was 2-3 at.% in the oxide films and the nitrogen atoms were concentrated at the interface region. This is consistent with the results obtained from (111)-oriented surfaces described above. The spectra was deconvoluted into three components using binding energy data with bonding at 398.2 eV, 399.7 eV and an unidentified bonding at 401.7 eV. The lowest energy peak at 398.2 eV can be assigned to the chemical environment of N similar to that of Si₃N₄, i.e., one nitrogen atom bonded to three Si atoms and may be designated as Si-N in **Fig. 5-13**. The second peak has a similar energy position to those found at the interfaces formed by FA³²⁾ and RTA³³⁾ thermal oxidation processes in N₂O ambient. Bhat *et al.*²⁶⁾ suggested that the peak at 399.7 eV corresponds to the Si₂=N-O bond, where one nitrogen atom is bonded to two Si and one O atom. On the other hand, Hussey *et al.*³²⁾ reported that a similar peak was found at the Si/SiO₂ interface formed by FA oxidation using N₂O gas and that it originates from N-Si-O bond where the nitrogen atom is partially replaced by O atom. In fact, the possibility

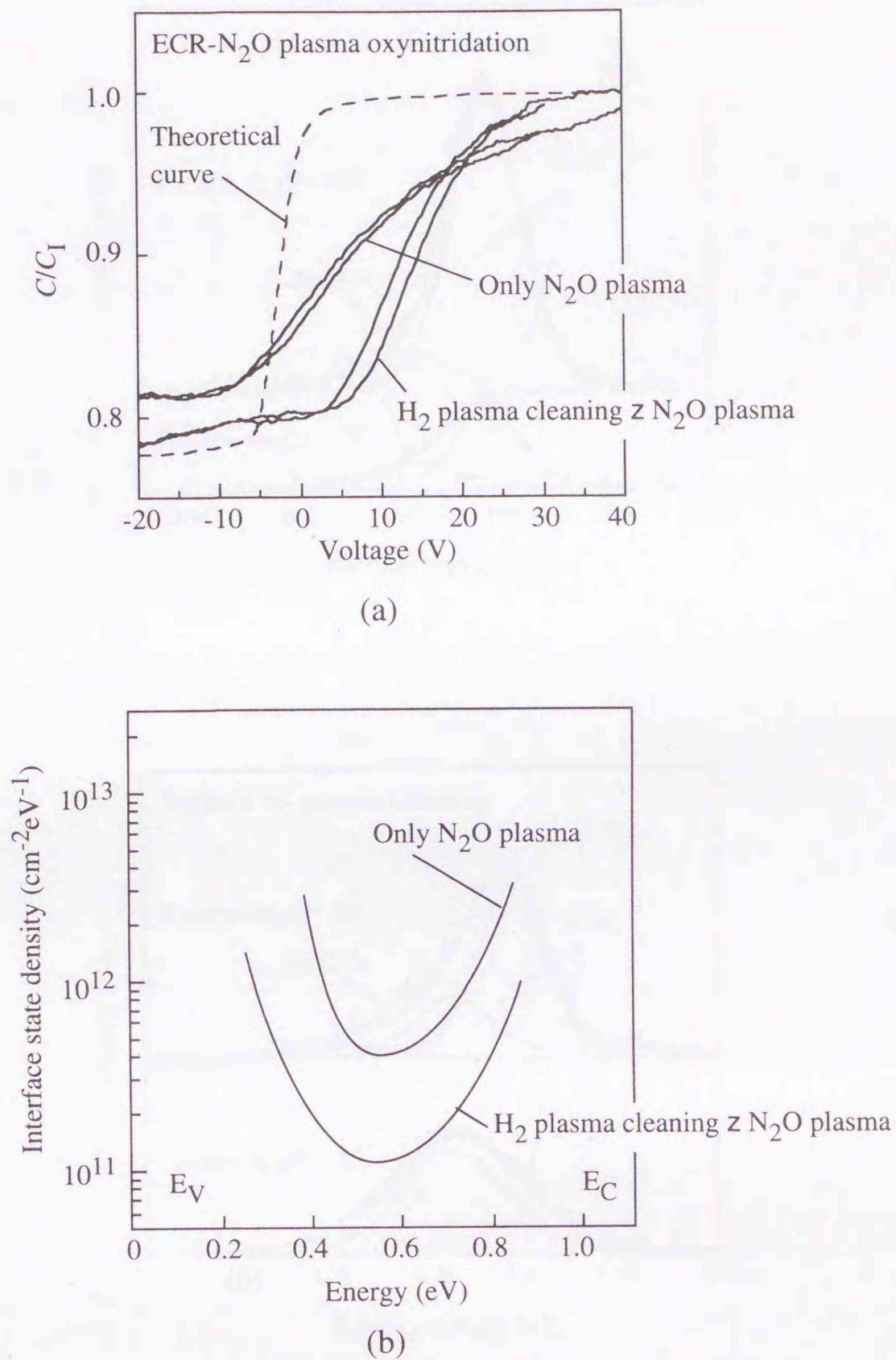
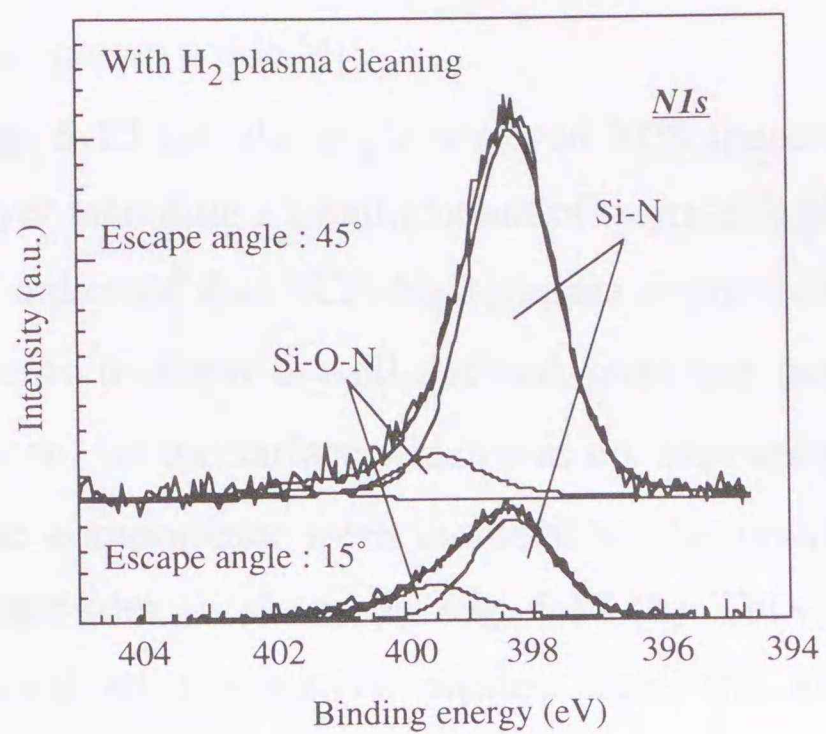
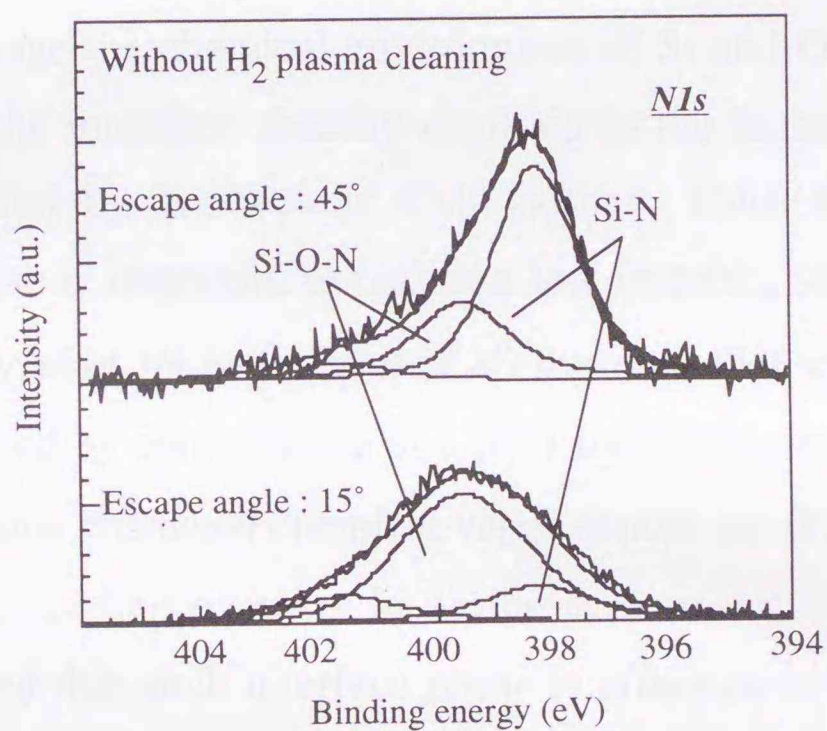


Fig. 5-12 (a) Contactless C - V curves taken on ECR- N_2O plasma oxynitridized surfaces with/without H_2 plasma cleaning process. (b) Calculated interface state density distributions.



(a)



(b)

Fig. 5-13 Angle-resolved XPS spectra of the N1s core-levels for ECR-N₂O plasma oxynitridized surface (a) with and (b) without H₂ plasma cleaning process.

of such bonding was predicted by the analysis of the infrared absorption (IR) spectra obtained from the N_2O -grown oxide.³⁴⁾

As shown in **Fig. 5-13 (a)**, the angle-resolved XPS spectra clearly indicate the presence of nitride layer including a small amount of oxynitride phase, being localized at the interface. This indicated that ECR- N_2O plasma oxynitridation after H_2 plasma cleaning process seems to form a well-defined interface configuration of $\text{SiO}_2/\text{Si}_3\text{N}_4/\text{Si}$. In comparison, for the surface which was not exposed to H_2 plasma, a large amount of oxynitride components were included at the interface and distributed throughout the insulator film, as shown in **Fig. 5-13 (b)**. Thus, it can be speculated that complete removal of the native oxides from the surface prior to the oxynitridation process is imperative for formation of a phase separated $\text{SiO}_2/\text{Si}_3\text{N}_4/\text{Si}$ structure, otherwise, during oxynitridation they may play a significant role for formation of large amount of oxynitrided components. Such complicated chemical statuses likely to change the chemical environment of Si and O atoms and to leave disordered bonds at the interface, thereby resulting in the higher value of interface state density measured by contactless C - V method. Thus, the phase separated $\text{SiO}_2/\text{Si}_3\text{N}_4/\text{Si}$ structure is important to realize a low interface state density value. In this regard, Lucovsky *et al.*¹⁶⁾ and Lee *et al.*³⁵⁾ reported that such phase-separated structure can be realized by combine use of a N_2O remote-plasma-assisted oxidation of Si surface and plasma enhanced chemical vapor deposition (PECVD) of thin SiO_2 film and are effective for improvement in device performance and reliability. Lu *et al.*²⁷⁾ recently reported that such interface phase is effective to reduce the interface strain due to a mismatch in a Si atomic density. Such an effect may be one of the possible reasons for improvement in the property of the interface formed by the ECR- N_2O plasma process.

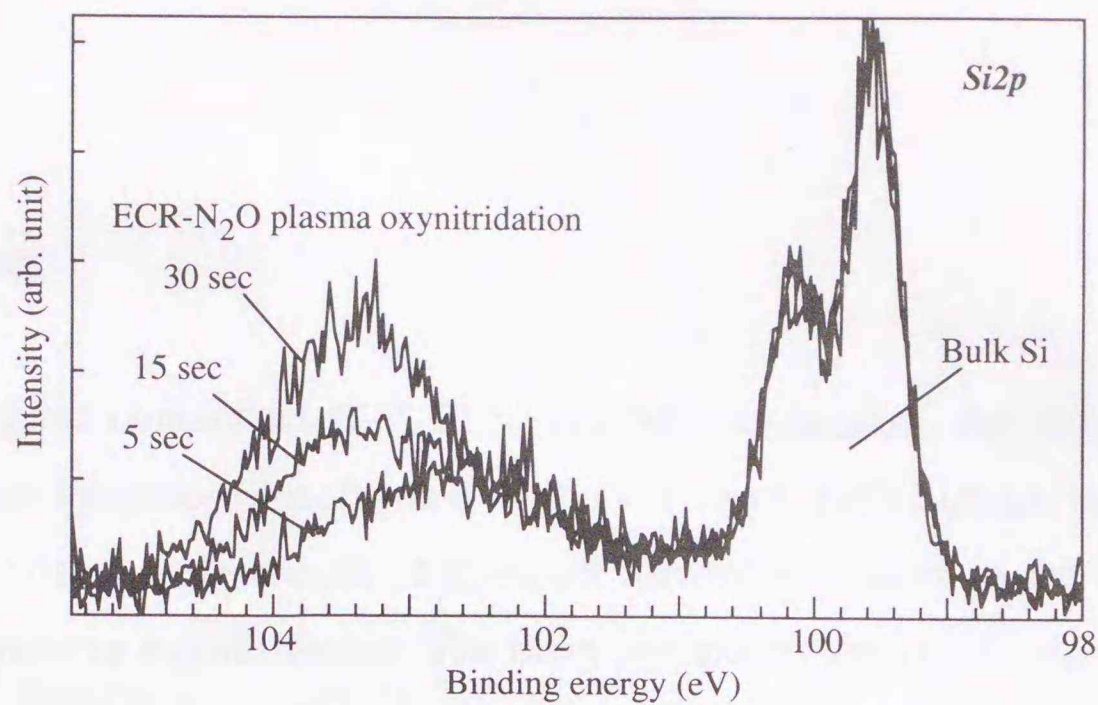
5. 3. 6 Study of initial stage of ECR- N_2O plasma oxynitridation

For the further investigation of mechanism of ECR- N_2O plasma oxynitridation,

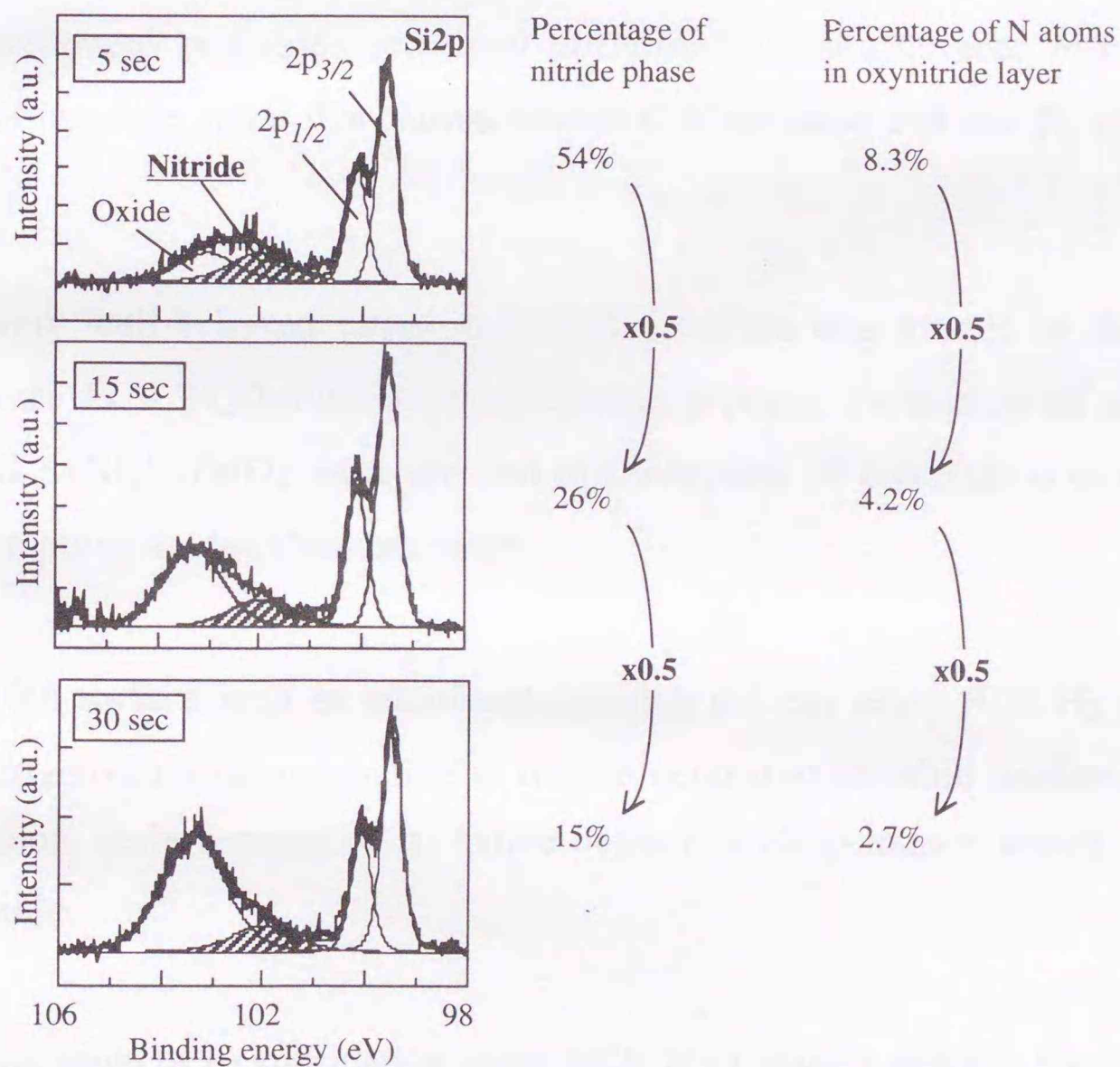
the initial stage of oxynitridation was studied by XPS.

Figure 5-14 (a) shows the XPS Si2p spectra of Si (111) surfaces after ECR-N₂O plasma oxynitridation. The exposing time were 5 sec, 15 sec and 30 sec. The height of the main Si peak corresponding to Si-Si bond were adjusted for each oxynitridation time. It can be seen that, at first, the nitride phase was appeared at around 102.4 eV after 5 sec treatment, then the oxide phase was grown. To make sure the origin of this peak appeared at around 102.4 eV, this peak was separated and compared with the percentage of N atoms in the oxynitride layer (**Fig. 5-14 (b)**). The integrated intensities of the peaks at around 102.4 eV were almost same values each other. The percentages of this peak in the oxynitride layer were 54%, 26% and 15% for the treatment time of 5 sec, 15 sec and 30 sec, respectively. And the calculated percentages of N atoms were 8.3%, 4.2% and 2.7%, respectively, as shown in **Fig. 5-14 (b)**. The ratio of variation of integrated intensity of the peak at around 102.4 eV from the treatment time of 5 sec to 15 sec was 0.5, and that of percentage of N atoms was also 0.5. Similarly, the ratio of variation of integrated intensity of the peak at around 102.4 eV from the treatment time of 15 sec to 30 sec was 0.6, and that of percentage of N atoms was also 0.6. Thus, the change of this peak at around 102.4 eV showed good agreement with the change of the percentage of N atoms in oxynitride layer. These results indicate that the nitride phase was firstly formed at the initial stage of oxynitridation, then the oxide phase was grown.

However, as described before, the interface structure was Si/Si-nitride/Si-oxide after enough time treatment. To form this structure, in spite of the earlier formation of nitride phase, the Si atoms had to go over the nitride phase being oxidized, or Si atoms were oxidized at the interface being in place of nitride phase. The detail is not clear yet, anyway, the nitride phase which is important to improve the interface properties is formed at the first stage of ECR-N₂O plasma oxynitridation. The residual oxide affected to form this nitride phase at the initial stage, which disturbed to create an abrupt Si/Si₃N₄/SiO₂ separation forming Si-oxynitride phase, as described in Sec. 5.3.5.



(a)



(b)

Fig. 5-14 (a) XPS Si2p spectra at the first stage of oxynitridation by ECR-N₂O plasma. A nitride phase was appeared at around 102 eV. And (b) the percentage of this nitride phase and the N atoms in oxynitride layer was compared with different oxynitridation time; 5 sec, 15 sec and 30 sec.

5.4 Summary

By using the contactless C - V , PLS³ and XPS techniques, the electronic properties of ultrathin-insulator films formed on Si (111) and (100) surfaces were systematically characterized. A hydrogen terminated surface was used as the initial surface prior to oxidation or oxynitridation. The main summaries are as follows.

- (1) Both low-temperature (400°C) thermal oxidation and subsequent ECR N_2 -plasma-treatment processes produced ultrathin- SiO_2/Si interfaces with a high density of interface states that caused limited C - V variation and low PL efficiency.
- (2) A relatively well-behaved ultrathin- SiO_2/Si interface was formed by the low-temperature ECR N_2O -plasma-oxynitridation process. Formation of a phase separated $Si/Si_3N_4/SiO_2$ structure and the reduction of suboxide components seem to improve the interface properties.
- (3) The Si(100) surface with an additional cleaning process using ECR- H_2 plasma is very attractive for understanding as well as control of ultrathin insulator films on an atomic scale because of its native-oxide-free clean nature, which is well reproducible.
- (4) At the first stage of oxynitridation using ECR- N_2O plasma process, the nitride-phase was formed at first, then the oxide component was grown.

References

- 1) K. Ohnishi and T. Hattori: Jpn. J. Appl. Phys. **33** (1994) L675.
- 2) R. S. Becker, G. S. Higashi, Y. J. Chabal and A. J. Becker: Phys. Rev. Lett. **65** (1990) 1917.
- 3) Y. Morita, K. Miki and H. Tokumoto: Appl. Phys. Lett. **59** (1991) 2187.
- 4) A. Ourmazd and P. H. Fuoss: Appl. Surf. Sci. **41/42** (1989) 365.
- 5) G. S. Higashi, Y. J. Chabal, G. W. Trucks and K. Raghavachari: Appl. Phys. Lett. **56** (1990) 656.
- 6) T. Takahagi, I. Nagai, A. Ishitani, H. Kuroda and Y. Nagasawa: J. Appl. Phys. **64** (1988) 3516.
- 7) S. Koyanagi, T. Hashizume and H. Hasegawa: Jpn. J. Appl. Phys. **35** (1996) 630.
- 8) T. Hashizume, S. Koyanagi and H. Hasegawa: J. Vac. Sci. Technol. **B14**(1996) 2872.
- 9) T. Hori, H. Iwasaki and K. Tsuji: IEEE Trans. Electron Devices **36** (1989) 340.
- 10) H. Fukuda, M. Yasuda, T. Iwabuchi and S. Ohno: IEEE Electron Dev. Lett. **EDL-12** (1991) 587.
- 11) G.W. Yoon, A.B. Joshi, J. Kim and D.L. Kwong: IEEE Electron Dev. Lett. **EDL-14** (1993) 179.
- 12) H. Hwang, W. Ting, B. Maiti, D.L. Kwong and J. Lee: Appl. Phys. Lett. **57** (1990) 1010.
- 13) H. Fukuda, T. Arakawa and S. Ohno: Jpn. J. Appl. Phys. **29** (1990) L2333.
- 14) T. Yoshida, T. Hashizume and H. Hasegawa: Jpn. J. Appl. Phys. **36** (1997) 1453.
- 15) D.R. Lee, C.G. Parker, J. R. Hauser and G. Lucovsky: J. Vac. Sci. & Technol. **B13** (1995) 1788.
- 16) G. Lucovsky, D.R. Lee, S.V. Hattangady, H. Niimi, Z. Jing, C. Parker and J. R. Hauser: Jpn. J. Appl. Phys. **34** (1995) 6827.
- 17) S. Chakraborty, T. Yoshida, T. Hashizume, H. Hasegawa and T. Sakai: J. Vac. Sci. Technol. **B16-4** (1998) 2159.
- 18) H. Hasegawa and H. Ohno: J. Vac. Sci. Technol. **B4** (1986) 1130.

- 19) J. Tersoff: Phys. Rev. B **30** (1984) 4874.
- 20) G. Lucovsky, Z. Jing and D. R. Lee: J. Vac. Sci. Technol. **B4** (1996) 2832.
- 21) F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff and G. Hollinger: Phys. Rev. B **38** (1988) 6084.
- 22) F. J. Himpsel, P. Heimann, T.-C. Chiang and D. E. Eastman: Phys. Rev. Lett. **45** (1980) 1112.
- 23) F. J. Himpsel, G. Hollinger and R. A. Pollak: Phys. Rev. B **28** (1983) 7014.
- 24) T. Yoshida and H. Hasegawa: Jpn. J. Appl. Phys. **39** (2000) 4504.
- 25) J. A. Taylor: Appl. Surf. Sci. **7** (1981) 168.
- 26) M. Bhat, G. W. Yoon, D. L. Kwong, M. Arendt and J. M. White: Appl. Phys. Lett. **64** (1994) 2116.
- 27) Z. H. Lu, R. J. Hussey, M. J. Graham, R. Cao and S. P. Tay: J. Vac. Sci. Technol. **B14** (1996) 2882.
- 28) C. J. Karlsson, F. Owman, E. Landemark, Y. C. Chao, P. Martensson and R. I. G. Uhrberg: Phys. Rev. Lett. **27** (1994) 4145.
- 29) K. Yamamoto and M. Hasegawa: J. Vac. Sci. Technol. **B12** (1994) 2493.
- 30) C. H. Bjorkman, J. L. Alay, H. Nishimura, M. Fukuda, T. Yamazaki and M. Hirose: Appl. Phys. Lett. **67** (1995) 2049.
- 31) T. Aiba, K. Yamauchi, K. Shimizu, N. Tate, M. Katayama and T. Hattori: Jpn. J. Appl. Phys. Part 1 **34** (1995) 707.
- 32) R. J. Hussey, T. L. Hoffman, Y. Tao and M. J. Graham: J. Electrochem. Soc. **143** (1996) 221.
- 33) E. C. Carr and R. A. Buhrman: Appl. Phys. Lett. **63** (1993) 54.
- 34) P. Lange, H. Bernt, E. Kartmannsgruber and F. Naumann: J. Electrochem. Soc. **141** (1994) 259.
- 35) D. R. Lee, G. Lucovsky, M. S. Denker and C. Magee: J. Vac. Sci. Technol. **A13** (1995) 1671.

Chapter 6 Conclusions

The purpose of this study is characterization of clean and passivated silicon surfaces based on ultrahigh-vacuum (UHV) contactless capacitance-voltage (C - V) measurements. Here, hydrogen terminated surface was used as a clean Si surface. And, in this study, oxidation and oxynitridation were used to passivate Si surfaces. The main conclusions are as follows.

In *Chapter 3*, a novel characterization method of electronic properties of semiconductor surfaces based on ultrahigh-vacuum (UHV) contactless capacitance-voltage (C - V) measurement method has been introduced. Detail explanation of principle and measurement system were also described. This method has been shown to be very powerful for *in-situ* electronic characterization of "free" and/or "processed" semiconductor surfaces. The conclusions of this chapter are ,

- (1) By introducing a narrow "UHV-gap" between the sample surface and the field electrode, many problems associated with the MIS C - V technique can be circumvented, such as tunneling current transport by thinning down of insulating layer, labor for electrode deposition which may destroy the intrinsic surface/interface characteristics just after processing step, considering the leakage current, and so on.
- (2) The UHV-gap length, one important parameter to analyze the measured C - V curves, can be determined accurately by measuring the variation of reflectance of laser light due to the Goos-Hächen effect. The possible existence of a surface layer of a thickness of 5 nm does not cause large errors.
- (3) Conduction type, carrier concentration, surface Fermi level position and surface/interface state density distribution can be determined quantitatively for various kinds of pre- and post processed semiconductor surfaces.
- (4) This UHV contactless C - V measurement system is connected to UHV-based multi-

chamber-system, which leads *in-situ* characterization after various kinds of processing steps such as plasma treatment, chemical vapor deposition (CVD), molecular beam epitaxy (MBE) growth, UHV annealing, ... without exposing into the air.

In **Chapter 4**, the hydrogen terminated Si surfaces were characterized using x-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM), UHV contactless (*C-V*) method and photoluminescence surface state spectroscopy (PLS³). The conclusions of this chapter are,

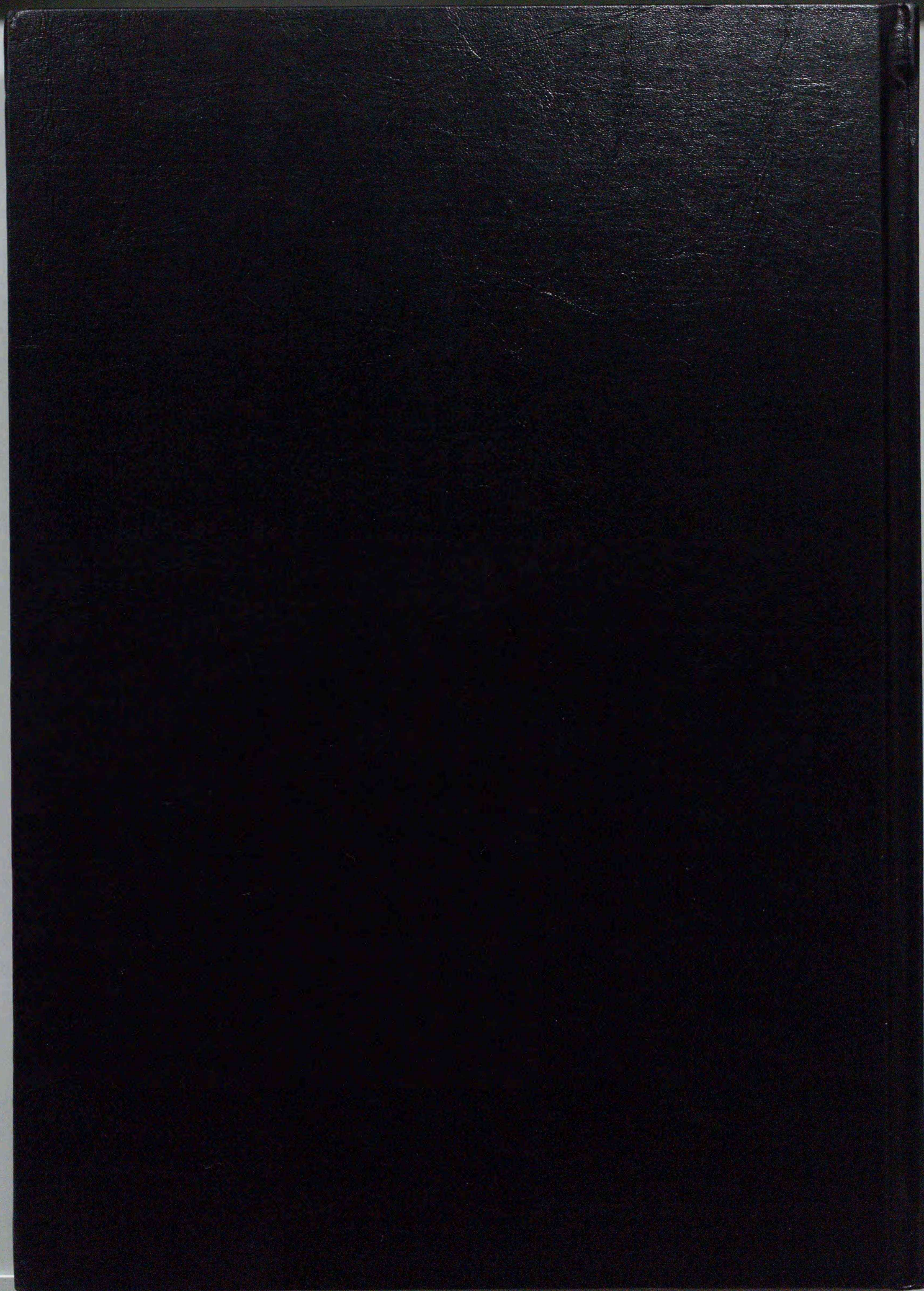
- (1) By dipping the Si(111) wafer into NH₄F solution, atomically clean and flat surface with terrace-step structure could be obtained, while the surface became atomically roughened after the treatment in HF solution. The terrace-step pattern shows the variety depending on the light intensity or the treatment time in NH₄F solution.
- (2) Hydrogen terminated Si surfaces possess fast surface states which has a discrete peak at 0.6-0.7 eV from valence band edge. They also possess slow states which causes hysteresis in *C-V* curves.
- (3) By the sufficiently long NH₄F treatment, the discrete states disappeared, and the hysteresis in *C-V* curve drastically reduced after UHV anneal at 200 °C. Thus, a UHV-compatible completely passivated surface could be obtained. Such surface seems to be thermally stable up to 250°C.
- (4) The most likely origin of fast surface states is Si-dangling bond, and that of slow surface states is excess hydrogen.

In **Chapter 5**, the electronic properties of ultrathin-insulator films formed on Si (111) and (100) surfaces were systematically characterized by using the UHV contactless *C-V*, PLS³ and XPS techniques. A hydrogen terminated surface was used as the initial surface prior to oxidation or oxynitridation. The conclusions of this chapter are,

- (1) Both low-temperature (400°C) thermal oxidation and subsequent ECR N₂-

plasma-treatment processes produced ultrathin-SiO₂/Si interfaces with a high density of interface states that caused limited *C-V* variation and low PL efficiency.

- (2) A relatively well-behaved ultrathin-SiO₂/Si interface was formed by the low-temperature ECR N₂O-plasma-oxynitridation process. Formation of a phase separated Si/Si₃N₄/SiO₂ structure and the reduction of suboxide components seem to improve the interface properties.
- (3) The Si(100) surface with an additional cleaning process using ECR-H₂ plasma (after the wet chemical treatment) is very attractive for understanding as well as control of ultrathin insulator films on an atomic scale because of its native-oxide-free clean nature, which is well reproducible.
- (4) At the first stage of oxynitridation using ECR-N₂O plasma process, the surface reaction started at the step-edge region. And the nitride-phase was formed at first, then the oxide component was grown.

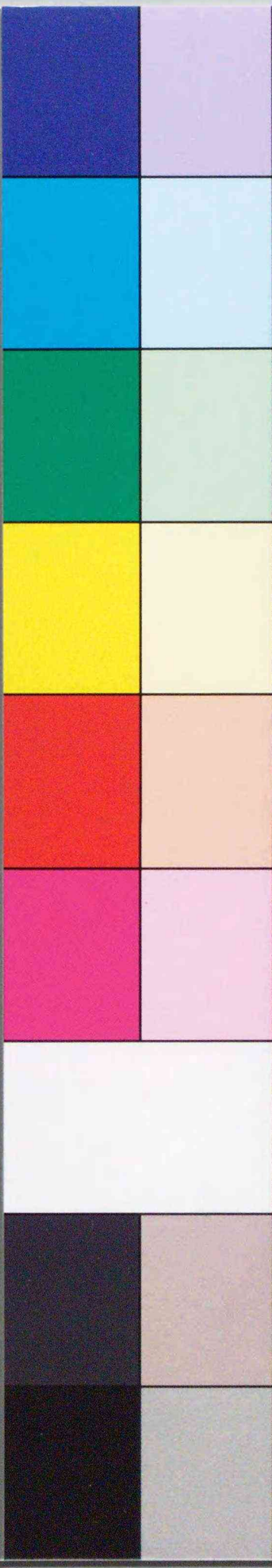




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