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Characterization of Dielectric-Silicon Structure by Photoreflectance Spectroscopy

フォトレフレクタンス分光法による誘電体-シリコン構造の評価に関する研究

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Abstract

Dielectric thin film/Si structures have been characterized by photoreflectance spectroscopy (PRS). The relationship between PRS spectrum and basic property of the dielectric film has been theoretically studied. The shape of PRS spectrum varies by light interference in thick (> 100 nm) and high refractive dielectric film in insulator/Si structure. PRS spectral intensity is expressed as a function of Si surface potential in insulator/Si structure. Since Si surface potential depends upon thickness and dielectric constant of dielectric film, they can be characterized by PRS spectral intensity.

SiO$_2$/Si structures have been characterized by PRS. $E_1$ critical point obtained by PRS spectrum linearly decreases with increasing tensile stress at surface of Si diaphragm structure. The growth of native Si oxide has been monitored by PRS. PRS spectral intensity increases and $E_1$ critical point decreases with growth of native oxide. This suggests that Si surface stress increases with growth of native oxide. From these results, a model of native oxidation mechanism has been suggested from discussion of PRS spectrum change. Moreover, thermally-oxidized SiO$_2$/Si structures have been also evaluated. The tensile stress at Si surface decreases with increasing temperature of thermal oxidation.

The dielectric films which have higher dielectric constant (high-$k$ films) have been characterized by PRS. The high-$k$ films (HfO$_2$, PrO$_x$) were mainly prepared by pulsed laser deposition (PLD). It is found that PRS spectral intensity is reduced by existence of positive charges caused by oxygen vacancy in high-$k$ film. The suitable deposition and rapid thermal annealing (RTA) conditions of high-$k$ films have been investigated. PRS spectral intensity becomes small in the case of deposition in N$_2$ atmosphere because of existence of large positive charge in the film. Moreover, the spectral intensity increases with increasing deposition temperature. It is considered that high-$k$ films which have higher dielectric constant is obtained for deposition at higher temperature. PRS spectral intensity of high-$k$/Si treated by RTA in N$_2$ and O$_2$ at 600°C is the largest. At more than 600°C, the interfacial layer growth reduces dielectric constant so that PRS spectral intensity decreases. As a result, it is considered that 600°C is suitable temperature for RTA in N$_2$ or O$_2$ atmosphere.

Metal-ferroelectric-insulator-semiconductor (MFIS) structures have been characterized by PRS.
SrBi$_2$Ta$_2$O$_9$ (SBT) was used for the ferroelectric material in this study. It is found that PRS spectral intensity is closely related to the ferroelectricity of SBT film. PRS spectral intensity increases after poling process by negative voltage. It is considered that Si surface potential is increased by remanent polarization in SBT film, so that the memorized states of MFIS structure can be characterized by PRS. PRS spectral intensity gradually decreases with increasing retained time of SBT/SiO$_2$/Si after poling. Decrease of the spectral intensity is suppressed by introducing RTA in deposition process. This result means that retention property of SBT/SiO$_2$/Si structure is improved by RTA.
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This work has been done at Okuyama Laboratory, Electronic Information Device Group, Area of Solid State Electronics, Division of Advanced Electronics and Optical Science, Department of Systems Innovation, Graduate School of Engineering Science, Osaka University.

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Masayuki SOHGAWA
Contents

Abstract i

Acknowledgments iii

1 Introduction 1
  1.1 Background ................................................. 1
    1.1.1 Technology Roadmap for Semiconductors and Introduction of High-k
          Materials ............................................. 1
    1.1.2 Ferroelectric Random Access Memory .......................... 3
    1.1.3 Modulation Spectroscopy and Photoreflectance Spectroscopy ....... 4
  1.2 Purpose of This Work ....................................... 5

2 Photoreflectance Spectroscopy 9
  2.1 Introduction ............................................... 9
  2.2 Franz-Keldysh Effect ...................................... 9
  2.3 Third Derivative Theory .................................. 13
  2.4 Relation between Reflectance and Dielectric Function .............. 15
    2.4.1 Normal Incidence ..................................... 15
    2.4.2 Oblique Incidence .................................... 16
    2.4.3 Incidence from Multiple Layers .......................... 20
    2.4.4 Complex Form of Reflectance ......................... 25
    2.4.5 Dependence of PRS Spectrum on Thickness and Refractive Index of Film 26
  2.5 Spectral Intensity of Photoreflectance ........................ 28
    2.5.1 Relation of PRS spectral intensity to Built-in Surface Potential .... 28
    2.5.2 Effect of Thickness and Dielectric constant of Dielectric film on Si .... 30
  2.6 Experiment of Photoreflectance ................................ 33
  2.7 Summary ................................................... 36
3 Characterization of SiO₂/Si Structure

3.1 Introduction .......................................................... 39
3.2 Measurement of Si Surface Stress by using Si Diaphragm ................. 39
  3.2.1 Sample Preparation ............................................. 39
  3.2.2 Strain estimation by elastic analysis ................................ 40
  3.2.3 Relation between PRS spectrum and Stress at Si Diaphragm Surface .... 41
3.3 Monitoring of Native Oxide Growth ....................................... 45
  3.3.1 Experimental Procedures ........................................ 45
  3.3.2 PRS Spectral Intensity with Native Oxide Growth ................. 45
  3.3.3 Increase of Tensile Stress by Native Oxide Growth ............... 47
3.4 Characterization of Thermal Oxidation .................................... 50
  3.4.1 Experimental Procedure ......................................... 50
  3.4.2 Stress at Interface between Si and Thermal Oxide ............... 50
  3.4.3 Dependence of PRS Spectral Intensity on SiO₂ Thickness ........... 52
3.5 Summary ............................................................... 52

4 Characterization of High-κ/Si Structures ................................. 57

4.1 Introduction .......................................................... 57
4.2 Sample Preparation .................................................... 58
  4.2.1 Pulsed Laser Deposition Method .................................. 58
  4.2.2 Metal Organic Decomposition Method ............................ 58
  4.2.3 RTA Treatment .................................................. 58
4.3 Excimer Laser Irradiation Effect ........................................ 61
4.4 HfO₂/Si Structure ........................................................ 64
  4.4.1 Deposition Condition Dependence .................................. 64
  4.4.2 RTA Condition Dependence ....................................... 66
4.5 PrOₓ/Si Structure ........................................................ 71
  4.5.1 Deposition Condition Dependence .................................. 71
  4.5.2 RTA Condition Dependence ....................................... 71
4.6 Other High-κ Materials .................................................. 75
4.7 Summary ............................................................... 75

5 Characterization of MFIS Structure ......................................... 81

5.1 Introduction .......................................................... 81
5.2 Sample Preparation and Characterization ................................... 81
5.3 PRS Spectrum of FIS Structure ........................................... 83
5.4 Memorized States of MFIS Capacitor ..................................... 86
Chapter 1

Introduction

1.1 Background

1.1.1 Technology Roadmap for Semiconductors and Introduction of High-$k$ Materials

Semiconductor devices are the basis to support our comfortable lives. They are incorporated in not only personal computers but also so many products such as mobile phones [1], home electric appliances [2] and cars [3]. A card and a tag which contain the integrated circuit (IC), so called IC card and IC tag, respectively, have already be realized to practical use today.

These applications have been allowed by a development of fine fabrication and high-integration technologies. The bipolar transistor was invented by Shockley, Brattain and Bardeen in 1947 [4]. Since then, semiconductor devices have been used for the amplifying and switching device instead of vacuum tubes. Moreover, integration of device elements has been explosively enhanced since invention of IC by Kilby in 1958 [4], and it has allowed higher-speed, lower-cost and lower power consumption for devices. Consequently, the semiconductor industry has been one of key industries in many contries as well as Japan.

However, there is “walls” for a development of more high-integrated circuit in the present day. Among their “walls”, it is the big issue that the thickness of the gate insulator of field-effect-transistor (FET) will become sub-nm order so that the leakage current through the gate by the direct tunneling effect will be not negligible and the reliability of devices will decrease by diffusion of boron atoms as the dopant. Consequently, it is studied that Materials which have higher dielectric constant($k$) than SiO$_2$ ($k = 3.9$), which called high-$k$ materials, will be employed for the gate insulator instead of SiO$_2$, to increase the gate thickness as keeping the same gate capacitance. Figure 1.1 shows trends of the gate leakage current density limit and simulated gate leakage due to direct tunneling current for (a) low standby power (LSTP), (b) low operating power (LOP) and (c) high-performance (HP) logic technologies, shown in the International Technology Roadmap for
Figure 1.1: Gate leakage current density limit and simulated gate leakage due to direct tunneling for (a) LSTP, (b) LOP and (c) HP logic technologies [5].
1.1 Background

Semiconductors (ITRS) 2003 [5]. The direct tunneling current will cross over the leakage current limit in 2006 for LSTP or LOP and in 2007 for HP logic technology. Thus, introduction of high-$k$ material is the pressing issue for the semiconductor industry. For high-$k$ gate oxide material, ZrO$_2$ [6, 7], HfO$_2$ [8, 9], and lanthanoid oxides [7, 10, 11] have been investigated because of their stability to silicon substrate and high permittivity. In particular, HfO$_2$ and and their silicates [12] or aluminates are promised for gate oxides.

However, the high-$k$ material is heterogeneous with silicon and must be physically deposited on the substrate so that it has various difficulties compared with SiO$_2$. Firstly, the interfacial layer between high-$k$ dielectric film and silicon substrate is grown by chemical reaction and it has lower dielectric constant. Secondly, its barrier height toward carriers is usually lower than SiO$_2$. Moreover, it has more fixed charge and interface states. Thirdly, it has small thermal-stability so that it crystallize during high-temperature processes. Studies in search for an solution of these difficulties are performed around the world.

### 1.1.2 Ferroelectric Random Access Memory

As described above, a development of finer fabrication and high-integration technologies is approaching physical limits. Therefore, novel devices will be needed in the future instead of complementary metal-oxide-semiconductor (CMOS) devices. It is mentioned in ITRS2003 [5] that post-CMOS devices must be addressed.

The ferroelectric random access memory (FeRAM) has been expected as a memory device instead of the dynamic random access memory (DRAM). Ferroelectrics have permanent dipole moments and a polarization that is not necessarily zero when there is no electric field [13]. The direction of a polarization can be controlled by external electric field. It can be applied to a non-volatile memory by corresponding direction of a polarization to an binary information which is “0” or “1”, because directed polarization is hold until applying electric field again. FeRAM is classified in two types [14]. One is an one transistor and one capacitor (1T/1C) type, which is like DRAM structure, as shown Fig. 1.2 (b). Although it has already been partly-put to practical use, scalability is similar to DRAM. Additionally, data is destructed when it is read out, similar

![Device structure of FeRAMs](image-url)
to DRAM. Second one is metal-ferroelectric-insulator-semiconductor (MFIS) -FET (1T) type, as shown in Fig. 1.2 (a). It has no capacitor so that it have much scalability. Moreover, data can be read out without destruction (non-destructive read-out). However, the retention time of MFIS-FET memory becomes degraded according to some factors such as leakage current and the relaxation of ferroelectric polarization [15]. Characteristics of MFIS structure such as the retention time is closely related to properties of silicon surface. Therefore, characterization of properties of the silicon surface in MFIS structure is very important.

1.1.3 Modulation Spectroscopy and Photoreflectance Spectroscopy

Spectra of optical constants such as the absorption coefficient and reflectivity are required to investigate an electronic energy band structure of the solid material. These spectra are closely related to electron transitions excited by the external light so that the band edges of an energy band structure can be decided by analysis of them. For actual measurements, however, the spectrum includes information from many transitions so that the energy band structure are hardly analyzed under various circumstances.

Photoreflectance spectroscopy (PRS) is one of measurement methods called modulation spectroscopy. Modulation spectroscopy is measurement method of change of the optical spectrum modulated by external perturbation. Since this change is a differential form of the spectrum without perturbation, a spectrum which has emphatic change at band edges is obtained. Electric field (electro-optical effect), temperature (thermo-optical effect), pressure (piezo-optical effect) and wavelength are employed for the external perturbation. In the case of PRS, electric field is induced at the semiconductor surface by carrier generated by irradiation of the modulation light and


1.2 Purpose of This Work

As described in the previous section, the introduction of high-\(k\) films or ferroelectric films in FET has captured the attention in recent years. It is considered that investigation of characteristics of silicon surface under these films is very important for future devices. In this work, various dielectric materials, deposition conditions and processes have been evaluated by investigation of the energy band structure at silicon surface by mainly PRS. It has not been studied that PRS is applied to characterization of these dielectric thin films. Particularly, it is noticed that energy-shift of PRS spectrum and PRS spectral intensity correspond to Si surface stress and Si surface potential, respectively. The targeted dielectric materials are SiO\(_2\), high-\(k\) dielectrics (HfO\(_2\), PrO\(_x\), etc.) and ferroelectrics (SrBi\(_2\)Ta\(_2\)O\(_9\)). Si surface under these thin films is examined non-destructively and contactless with making full use of features of PRS. Conclusively, establishment of PRS as characterization tool of Si is aimed.

This work is organized into 6 chapters. The theories and the experimental method of PRS has been described in Chap. 2. The quantitative characterization of Si surface stress by PRS is described in Chap. 3. Thermally- or natively-grown SiO\(_2\)/Si structure is also discussed in Chap. 3. The deposition and annealing conditions of high-\(k\) films (high-\(k\) material: HfO\(_2\), PrO\(_x\), ZrO\(_2\), Al\(_2\)O\(_3\) and La\(_2\)O\(_3\)) are characterized and discussed in Chap. 4. Then in Chap. 5, the hysteresis
and retention properties of MFIS structures are characterized by PRS. Finally, the results from these studies are concluded in Chap. 6. The organization of this thesis is shown in Fig. 1.4.
Reference


Chapter 2

Photoreflectance Spectroscopy

2.1 Introduction

As described in Chap. 1, the study of modulation spectroscopy has a long history, and its theory has been already developed. However, in the case of PRS, it should be taken into account that the spectrum is affected by the surface potential of semiconductor, power and frequency of modulation light, the thickness and dielectric constant of the film and interference of probe light in the film. In this chapter, theories including these effects in addition to known theory are described. Moreover, actual PRS experiment in this work is also described.

2.2 Franz-Keldysh Effect

Schrödinger equation in relative coordinate system for electron-hole pair including the term of the static electric field \( E = [E_x, E_y, E_z] \) in the case of neglecting Coulomb interaction is expressed as following equation [1],

\[
\begin{bmatrix}
-\frac{\hbar^2}{2\mu} \nabla^2 - qE \cdot \mathbf{r} \\
\end{bmatrix} \phi(\mathbf{r}) = E\phi(\mathbf{r}),
\]

(2.1)

where \( \mu \) is a reduced effective mass tensor and \( E \) is a energy eigenvalue, respectively. Using components of vectors \( \mathbf{r} = [x, y, z] \), \( \nabla = \left[ \frac{d^2}{dx^2}, \frac{d^2}{dy^2}, \frac{d^2}{dz^2} \right] \), eq. (2.1) is expressed as a following equation,

\[
\begin{bmatrix}
-\frac{\hbar^2}{2\mu_x} \frac{d^2}{dx^2} - \frac{\hbar^2}{2\mu_y} \frac{d^2}{dy^2} - \frac{\hbar^2}{2\mu_z} \frac{d^2}{dz^2} - q\left(E_x x + E_y y + E_z z\right)
\end{bmatrix} \phi(x, y, z)

= E\phi(x, y, z),
\]

(2.2)

where \( \mu_i \) \( (i = x, y, z) \) are values of the principal direction of the reduced effective mass tensor. \( \phi(\mathbf{r}) \) can be separated \( \phi(x) \phi(y) \phi(z) \), and each of them is satisfied a following equation,

\[
\begin{bmatrix}
-\frac{\hbar^2}{2\mu_i} \frac{d^2}{dr_i^2} - qE_i r_i - E_i
\end{bmatrix} \phi(r_i) = 0,
\]

(2.3)
To solve this differential equation, a following variable transformation is performed,

\[ \theta_i = \sqrt{\frac{q^2 E_i^2 \hbar^2}{2 \mu_i}}, \]

(2.5)

\[ \xi_i = \frac{E_i + qE_i r_i}{\hbar \theta_i}. \]

(2.6)

Then eq. (2.3) is transformed into a following equation,

\[ \frac{d^2}{d\xi_i^2} \phi(\xi_i) = -\xi_i \phi(\xi_i). \]

(2.7)

The solution of eq. (2.7) is given by using Airy function [2].

\[ \phi(\xi_i) = C_i \text{Ai}(\xi_i), \]

(2.8)

where \( \text{Ai}(z) \) is defined as,

\[ \text{Ai}(z) = \frac{1}{\pi} \int_0^\infty \cos \left( \frac{1}{3} s^3 + sx \right) ds. \]

(2.9)

And \( C_i \) is a normalization constant of \( \phi(\xi) \),

\[ C_i = \sqrt{\frac{q |E_i|}{\hbar \theta_i}}. \]

(2.10)

Therefore, \( \phi(x, y, z) \) is expressed by a following equation,

\[ \phi(x, y, z) = C_x C_y C_z \text{Ai}(\xi_x) \text{Ai}(\xi_y) \text{Ai}(\xi_z). \]

(2.11)
2.2 Franz-Keldysh Effect

Figure 2.2: Calculated \( \varepsilon_2 \) with and without electric field vs. \( \eta = \frac{E - E_g}{\hbar \theta} \) near the M_0 critical point.

Figure 2.3: Calculated \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) for electric field modulation vs. \( \eta = \frac{E - E_g}{\hbar \theta} \) near the M_0 critical point.

Figure 2.1 shows a wave function (normalized by \( C_i \)) calculated from eq. (2.11) when \( \mathcal{E} = [E_x, 0, 0] \), \( k_y = k_z = 0 \) and \( E = 0 \). The wave function penetrates the area of \( x < 0 \) (\( \xi_x < 0 \)) so that optical transition becomes possible for the photon which has energy less than bandgap energy.

The imaginary part of the dielectric function \( \varepsilon_2 (E, \mathcal{E}) \) at the M_0 critical point with the electric field is expressed as a following equation [1],

\[
\varepsilon_2 (E, \mathcal{E}) = A \pi \left[ \text{Ai}^2 (-\eta) + \eta \text{Ai}^2 (-\eta) \right],
\]

(2.12)

where

\[
\eta = \frac{E - E_g}{\hbar \theta},
\]

(2.13)

\[
\theta = \left( \theta_x \theta_y \theta_z \right)^{\frac{1}{3}}.
\]

(2.14)

And the imaginary part of the dielectric function without field \( \varepsilon_2 (E, 0) \)

\[
\varepsilon_2 (E, 0) = A \sqrt{\frac{E - E_g}{\hbar \theta}},
\]

(2.15)

where

\[
A = \frac{q^2}{2 \pi m^2 \omega^2} \left| \mathbf{e} \cdot \mathbf{p} \right|^2 \sqrt{\frac{8 |\mu_x \mu_y \mu_z|}{\hbar^6}} \sqrt{\hbar \theta}.
\]

(2.16)

and \( |\mathbf{e} \cdot \mathbf{p}| \) is the matrix element of momentum. Figure 2.2 shows the imaginary part of dielectric function calculated for the M_0 critical point with and without electric field. The difference \( \Delta \varepsilon_2 (E, \mathcal{E}) \) is obtained as

\[
\Delta \varepsilon_2 (E, \mathcal{E}) = \varepsilon_2 (E, \mathcal{E}) - \varepsilon_2 (E, 0)
\]
\[
\begin{align*}
\Delta \varepsilon_2 (E, \varepsilon) &= AG (-\eta), \\
G (-\eta) &= \pi [Ai' (-\eta) Bi' (-\eta) + \eta Ai (-\eta) Bi (-\eta)] \\
&\quad + u (\eta) \sqrt{-\eta}.
\end{align*}
\]

Figure 2.3 shows calculated dielectric function from eqs. (2.17) and (2.19) for the M\(_0\) critical point. The difference becomes maximum value at critical point energy (\(\eta = 0\)). The oscillation appears at photon energy over critical point (\(\eta > 0\)). This oscillation is called Franz-Keldysh oscillation.
2.3 Third Derivative Theory

Under low electric field, the difference of dielectric function becomes a simple shape instead of the Franz-Keldysh oscillation. It was found by Aspnes that its shape is similar to third derivative of dielectric function, so its theory is called Aspnes's third derivative theory [1].

The dielectric functions for single critical point $E_g$ which is 1, 2 or 3 dimensional simple parabolic band are expressed as following equations considering broadening (broadening factor: $\Gamma$) [9],

$$
\varepsilon(E, \Gamma)_{1D} = \frac{Q D_y D_z l^{i+1}}{E^2} (E - E_g + i\Gamma)^{-\frac{1}{2}}
$$

$$
\varepsilon(E, \Gamma)_{2D} = \frac{Q D_y D_z l^{i+1}}{E^2} \ln (E - E_g + i\Gamma)
$$

$$
\varepsilon(E, \Gamma)_{3D} = \frac{2\pi Q D_y D_z l^{i+1}}{E^2} (E - E_g + i\Gamma)^{\frac{1}{2}},
$$

where

$$
Q = \frac{q^2 h^2}{\pi m} |e \cdot p|
$$

$$
D_j = \sqrt{\frac{2 |\mu_{jj}|}{\hbar^2}}, \quad j = x, y, z,
$$

$K_j = K_y$ or $K_z$ are the cutoff lengths in the Brillouin zone for 1 and 2 dimensional critical points, and $l$ shows the critical point type which is equal to the number of negative masses $\mu_{jj}$. These equations are shown as the generic form,

$$
\varepsilon(E, \Gamma) = A \Gamma^{-k} e^{i\theta} (E - E_g + i\Gamma)^k,
$$

$k$ depends upon the dimension of the critical point, is $-\frac{1}{2}$ for 1D, 0 (logarithmic) for 2D and $\frac{1}{2}$ for 3D.

When the electric field is enough low, the difference of dielectric function with electric field is the third derivative of dielectric function without electric field [23],

$$
\Delta \varepsilon(E, \Gamma, E) \propto \frac{E^2}{E^2} \frac{\partial^3}{\partial E^3} E^2 \varepsilon(E, \Gamma)
$$

Substituting (2.26) to (2.27), we obtain

$$
\Delta \varepsilon(E, \Gamma, E) = B E^2 e^{i\theta} (E - E_g + i\Gamma)^{k-3} = C e^{i\theta} (E - E_g + i\Gamma)^{-n},
$$

where $B$ and $C$ are constants and $n = -(k - 3)$ depends upon dimension of the critical point, is $\frac{7}{2}$ for 1D, 3 (logarithmic) for 2D and $\frac{5}{2}$ for 3D.

Figure 2.4 shows the imaginary part of dielectric function calculated by eq. (2.26) and its difference calculated by eq. (2.28) for 3D $M_0$ critical point. A simple spectrum mainly composed of two plus and minus peak is observed.
Figure 2.4: Imaginary part of dielectric function calculated by eq. (2.26) and its difference calculated by (2.28) for 3D M₀ critical point.
2.4 Relation between Reflectance and Dielectric Function

2.4.1 Normal Incidence

When the light enters from a transparent medium I (refractive index: \( n_1 = n_a \)) to a medium II (complex refractive index: \( n_\text{II} = n^* = n + ik \)) as shown in Fig. 2.5, the complex reflectivity, \( r^* \) and reflectance, \( R \) is expressed as a following equation [3],

\[
\begin{align*}
    r^* &= \frac{n_\text{II} - n_1}{n_\text{II} + n_1} = \frac{n^* - n_a}{n^* + n_a} \\
    R &= |r^*|^2 = \frac{|n^* - n_a|^2}{|n^* + n_a|^2} = \frac{(n - n_a)^2 + k^2}{(n + n_a)^2 + k^2}.
\end{align*}
\]

(2.29)

(2.30)

There are generally relationships between the complex refractive index and the relative complex dielectric constant, \( \varepsilon^* = \varepsilon_1 + i\varepsilon_2 \) (permability \( \mu \) equal to vacuum permability \( \mu_0 \) at any time) [3],

\[
    n^* = \sqrt{\varepsilon^*}.
\]

(2.31)

Substituting the refraction index of medium II to eq. (2.31),

\[
    \varepsilon_1 + i\varepsilon_2 = (n + ik)^2 = n^2 - k^2 + 2ink.
\]

(2.32)

Since the real and imaginary parts of both sides must equal, following relationships are obtained.

\[
\begin{align*}
    \varepsilon_1 &= n^2 - k^2 \\
    \varepsilon_2 &= 2nk \\
    n &= \sqrt{\frac{\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}} \\
    k &= \sqrt{-\varepsilon_1 + \frac{\varepsilon_1^2 + \varepsilon_2^2}{2}}.
\end{align*}
\]

(2.33)

(2.34)

(2.35)

(2.36)

As described in § 2.2, the dielectric constant is varied by the electro-optical effect, so the reflectance change \( \Delta R \) may be obtained as a total differential of \( R \) by using dielectric constants of all media. The total differential of eq. (2.30) is expressed as a following equation,

\[
    \Delta R = \frac{\partial R}{\partial \varepsilon_1} \Delta \varepsilon_1 + \frac{\partial R}{\partial \varepsilon_2} \Delta \varepsilon_2 + \frac{\partial R}{\partial \varepsilon_a} \Delta \varepsilon_a
\]

(2.37)

Assuming that the medium I is affected by the perturbation, \( \Delta \varepsilon_a \) is negligible. Thus, the third term of eq. (2.37) equal to zero, so that \( \Delta R \) can be expressed by an easy form,

\[
    \Delta R = \frac{\partial R}{\partial \varepsilon_1} \Delta \varepsilon_1 + \frac{\partial R}{\partial \varepsilon_2} \Delta \varepsilon_2.
\]

(2.38)
Therefore, the ratio of reflectance difference to reflectance, $\frac{\Delta R}{R}$ is expressed by the following equation,

$$\frac{\Delta R}{R} = \frac{1}{R} \frac{\partial R}{\partial \varepsilon_1} \Delta \varepsilon_1 + \frac{1}{R} \frac{\partial R}{\partial \varepsilon_2} \Delta \varepsilon_2$$

$$= \alpha (\varepsilon_1, \varepsilon_2) \Delta \varepsilon_1 + \beta (\varepsilon_1, \varepsilon_2) \Delta \varepsilon_2.$$  \hspace{1cm} (2.39)

where $\alpha (\varepsilon_1, \varepsilon_2)$ and $\beta (\varepsilon_1, \varepsilon_2)$ are called the Seraphin coefficients [4], expressed as following functions,

$$\alpha (\varepsilon_1, \varepsilon_2) = \frac{1}{R} \frac{\partial R}{\partial \varepsilon_1} = \frac{2\gamma}{\gamma^2 + \delta^2}$$  \hspace{1cm} (2.40)

$$\beta (\varepsilon_1, \varepsilon_2) = \frac{1}{R} \frac{\partial R}{\partial \varepsilon_2} = \frac{2\delta}{\gamma^2 + \delta^2},$$  \hspace{1cm} (2.41)

where,

$$\gamma = \frac{n}{n_a} \left( n^2 - 3k^2 - n_a^2 \right)$$  \hspace{1cm} (2.42)

$$\delta = \frac{k}{n_a} \left( 3n^2 - k^2 - n_a^2 \right).$$  \hspace{1cm} (2.43)

Figure 2.6 shows Seraphin coefficients $\alpha$ and $\beta$ of Si calculated by eqs. (2.40) and (2.41) by using reported complex refractive index [5]. The Seraphin coefficients give a relationship between the reflectance and the dielectric function.

### 2.4.2 Oblique Incidence

Now, the reflection in the case of oblique incidence is discussed. Figure 2.7 shows a model of oblique incidence with incident angle $\theta_i$ and refraction angle $\theta_t^*$ (a complex number, $\theta_t^* = \theta_{t1} + i\theta_{t2}$).
2.4 Relation between Reflectance and Dielectric Function

![Graph showing the relation between reflectance and dielectric function](image)

Figure 2.6: Calculated Seraphin coefficients of Si, $\alpha$ and $\beta$ as a function of photon energy. $n$ and $k$ value reported in ref. [5], and $n_a = 1$ are used for calculation.

The reflectivities, $r_s^*$ for s-polarized light and $r_p^*$ for p-polarized light are expressed as following equations, respectively [3],

\[
r_s^* = \frac{n_1 \cos \theta_i - n_{II} \cos \theta_i^*}{n_1 \cos \theta_i + n_{II} \cos \theta_i^*} = \frac{n_a \cos \theta_i - (n + ik) \cos \theta_i^*}{n_a \cos \theta_i + (n + ik) \cos \theta_i^*} \tag{2.44}
\]

\[
r_p^* = \frac{n_{II} \cos \theta_i - n_1 \cos \theta_i}{n_{II} \cos \theta_i + n_1 \cos \theta_i} = \frac{(n + ik) \cos \theta_i - n_a \cos \theta_i^*}{(n + ik) \cos \theta_i + n_a \cos \theta_i^*} \tag{2.45}
\]

There is a following relationship from Snell’s low,

\[
n_a \sin \theta_i = (n + ik) \sin \theta_i^*. \tag{2.46}
\]

Therefore,

\[
(n + ik) \cos \theta_i^* = (n + ik) \sqrt{1 - \sin^2 \theta_i^*} = \sqrt{(n + ik)^2 - \sin^2 \theta_i}. \tag{2.47}
\]

Substituting eq. (2.47) to eqs (2.44) and (2.45), we obtain

\[
r_s^* = \frac{n_a \cos \theta_i - \sqrt{(n + ik)^2 - \sin^2 \theta_i}}{n_a \cos \theta_i + \sqrt{(n + ik)^2 - \sin^2 \theta_i}} \tag{2.48}
\]

\[
r_p^* = \frac{(n + ik)^2 \cos \theta_i - n_a^2 \sqrt{(n + ik)^2 - \sin^2 \theta_i}}{(n + ik)^2 \cos \theta_i + n_a^2 \sqrt{(n + ik)^2 - \sin^2 \theta_i}} \tag{2.49}
\]
The reflectance $R_j$ ($j = s$ and $p$ for each polarized lights) is

$$
R_j = |r_j|^2 = \Re \left( r_j \right)^2 + \Im \left( r_j \right)^2.
$$

(2.50)

The Seraphin coefficients in eq. (2.39) are calculated as

$$
\alpha_j (\varepsilon_1, \varepsilon_2) = \frac{1}{R_j} \frac{\partial R_j}{\partial \varepsilon_1} = 2 \frac{\Re \left( r_j \frac{\partial r_j}{\partial \varepsilon_1} \right) + \Im \left( r_j \frac{\partial r_j}{\partial \varepsilon_1} \right)}{\Re \left( r_j \right)^2 + \Im \left( r_j \right)^2}.
$$

(2.51)

$$
\beta_j (\varepsilon_1, \varepsilon_2) = \frac{1}{R_j} \frac{\partial R_j}{\partial \varepsilon_2} = 2 \frac{\Re \left( r_j \frac{\partial r_j}{\partial \varepsilon_2} \right) + \Im \left( r_j \frac{\partial r_j}{\partial \varepsilon_2} \right)}{\Re \left( r_j \right)^2 + \Im \left( r_j \right)^2}.
$$

(2.52)

The differential forms of reflectance are shown as following equations,

$$
\frac{\partial r_j^s}{\partial \varepsilon_1} = \frac{-n_a \cos \theta_i}{\sqrt{(n + ik)^2 - \sin^2 \theta_i} \left[ n_a \cos \theta_i + \sqrt{(n + ik)^2 - \sin^2 \theta_i} \right]^2},
$$

$$
\frac{\partial r_j^s}{\partial \varepsilon_2} = \frac{-in_a \cos \theta_i}{\sqrt{(n + ik)^2 - \sin^2 \theta_i} \left[ n_a \cos \theta_i + \sqrt{(n + ik)^2 - \sin^2 \theta_i} \right]^2},
$$

$$
\frac{\partial r_j^p}{\partial \varepsilon_1} = \frac{n_a \cos \theta_i \left( (n + ik)^2 - 2 \sin^2 \theta_i \right)}{\sqrt{(n + ik)^2 - \sin^2 \theta_i} \left[ (n + ik)^2 \cos \theta_i + n_a \sqrt{(n + ik)^2 - \sin^2 \theta_i} \right]^2},
$$

$$
\frac{\partial r_j^p}{\partial \varepsilon_2} = \frac{in_a \cos \theta_i \left( (n + ik)^2 - 2 \sin^2 \theta_i \right)}{\sqrt{(n + ik)^2 - \sin^2 \theta_i} \left[ (n + ik)^2 \cos \theta_i + n_a \sqrt{(n + ik)^2 - \sin^2 \theta_i} \right]^2}.
$$

For unpolarized light, the reflectance $R$ is [6]

$$
R = \frac{1}{2} \left( R_s + R_p \right).
$$

(2.53)

Thus, Seraphin coefficients are shown as following equations,

$$
\alpha (\varepsilon_1, \varepsilon_2) = \frac{1}{R_s + R_p} \left( R_s \alpha_s + R_p \alpha_p \right)
$$

(2.54)

$$
\beta (\varepsilon_1, \varepsilon_2) = \frac{1}{R_s + R_p} \left( R_s \beta_s + R_p \beta_p \right).
$$

(2.55)

The calculated $\alpha$ and $\beta$ for unpolarized light are shown in Fig. 2.8. Obviously, the values for $\theta_i = 0^\circ$ (normal incident) are equal to that in Fig. 2.6. In the case of $\theta_i = 45^\circ$, it is exactly similar to that for $\theta_i = 0^\circ$ in this energy region. On the other hand, visible change is observed for $\theta_i = 75^\circ$. 


2.4 Relation between Reflectance and Dielectric Function

Medium I

\((\epsilon_1, n_1, \mu_0)\)

\(\theta_i\)

Medium II

\((\epsilon_2 + i\epsilon_3, n + ik, \mu_0)\)

\(\theta_t^*\)

\(r^*\)

Figure 2.7: An illustration of obliquely-incident light near interface between a medium I and a medium II.

\(\alpha\), \(\beta\)

Figure 2.8: Calculated spectra of Seraphin coefficients, \(\alpha\) and \(\beta\), for 0\(^\circ\), 45\(^\circ\) and 75\(^\circ\).
2.4.3 Incidence from Multiple Layers

In the case of incidence from thin (∼wavelength) multiple layers which have different refractive indices, the optical interference must be considered.

a) 1 Layer

The reflectivity is expressed as a following equation in the case of incidence through 1 layer which have refractive index \( n_a \) as shown in Fig. 2.9 [7].

\[
\begin{align*}
    r^* &= \frac{r_a + r_0^*e^{-i\Delta_a}}{1 + r_a r_0^*e^{-i\Delta_a}} \\
    \Delta_a &= \frac{2\pi d_a}{\lambda} n_a \cos \theta_a,
\end{align*}
\]

(2.56)

where

\[
\begin{align*}
    n_a \cos \theta_a &= n_a \sqrt{1 - \sin^2 \theta_a} = \sqrt{n_a^2 - \sin^2 \theta_i} \\
    (n + ik) \cos \theta_i^* &= (n + ik) \sqrt{1 - \sin^2 \theta_i^*} = \sqrt{(n + ik)^2 - \sin^2 \theta_i^*}
\end{align*}
\]

(2.57)

(2.58)

so there are the relation shown as following equations,

\[
\begin{align*}
    n_a \cos \theta_a &= n_a \sqrt{1 - \sin^2 \theta_a} = \sqrt{n_a^2 - \sin^2 \theta_i} \\
    (n + ik) \cos \theta_i^* &= (n + ik) \sqrt{1 - \sin^2 \theta_i^*} = \sqrt{(n + ik)^2 - \sin^2 \theta_i^*}
\end{align*}
\]

(2.59)

(2.60)

\( r_a \) and \( r_0^* \) (\( j = s \) or \( p \)) are the reflectivity at interface between the air and layer a and that between layer a and the substrate, respectively. These reflectivities are expressed as following equations,

\[
\begin{align*}
    r_{as} &= \frac{\cos \theta_i - n_a \cos \theta_a}{\cos \theta_i + n_a \cos \theta_a} \\
    &= \frac{\cos \theta_i - \sqrt{n_a^2 - \sin^2 \theta_i}}{\cos \theta_i + \sqrt{n_a^2 - \sin^2 \theta_i}} \\
    r_{0s}^* &= \frac{n_a \cos \theta_a - (n + ik) \cos \theta_i^*}{n_a \cos \theta_a + (n + ik) \cos \theta_i^*} \\
    &= \frac{\sqrt{n_a^2 - \sin^2 \theta_i}}{\sqrt{(n + ik)^2 - \sin^2 \theta_i}} \\
    r_{ap} &= \frac{n_a \cos \theta_i - \cos \theta_a}{n_a \cos \theta_i + \cos \theta_a} \\
    &= \frac{n_a^2 \cos \theta_i - \sqrt{n_a^2 - \sin^2 \theta_i}}{n_a^2 \cos \theta_i + \sqrt{n_a^2 - \sin^2 \theta_i}} \\
    r_{0p}^* &= \frac{(n + ik) \cos \theta_a - n_a \cos \theta_i^*}{(n + ik) \cos \theta_a + n_a \cos \theta_i^*}
\end{align*}
\]

(2.61)

(2.62)

(2.63)
2.4 Relation between Reflectance and Dielectric Function

\[
\frac{(n + ik)^2 \sqrt{n_a^2 - \sin^2 \theta_i} - n_n^2 \sqrt{(n + ik)^2 - \sin^2 \theta_i}}{(n + ik)^2 \sqrt{n_a^2 - \sin^2 \theta_i} + n_n^2 \sqrt{(n + ik)^2 - \sin^2 \theta_i}} \tag{2.64}
\]

The reflectance \( R_j \) is obtained by using eq. (2.56) as,

\[
R_j = \frac{r_{aj} + r_{0j}^* e^{-i2\Delta_0}}{1 + r_{aj}r_{0j}^* e^{-i2\Delta_0}} \]

\[
= \left| \frac{r_{aj} + r_{0j}^* e^{-i2\Delta_0}}{1 + r_{aj}r_{0j}^* e^{-i2\Delta_0}} \right|^2 \tag{2.65}
\]

\[
= \frac{\left[ r_{aj} + \Re \left( r_{0j}^* e^{-i2\Delta_0} \right) \right]^2 + \left[ \Im \left( r_{0j}^* e^{-i2\Delta_0} \right) \right]^2}{\left[ 1 + r_{aj} \Re \left( r_{0j}^* e^{-i2\Delta_0} \right) \right]^2 + \left[ r_{aj} \Im \left( r_{0j}^* e^{-i2\Delta_0} \right) \right]^2} \]

\[
= \frac{A_{1j}}{A_{2j}}, \tag{2.66}
\]

where

\[
A_{1j} = \left[ r_{aj} + \Re \left( r_{0j}^* e^{-i2\Delta_0} \right) \right]^2 + \left[ \Im \left( r_{0j}^* e^{-i2\Delta_0} \right) \right]^2 \tag{2.67}
\]

\[
A_{2j} = \left[ 1 + r_{aj} \Re \left( r_{0j}^* e^{-i2\Delta_0} \right) \right]^2 + \left[ r_{aj} \Im \left( r_{0j}^* e^{-i2\Delta_0} \right) \right]^2 \tag{2.68}
\]

The Seraphin coefficient \((j = s, p\) and \(k = 1, 2)\) is shown as

\[
1 \frac{\partial R_j}{R_j \partial \varepsilon_k} = \frac{\frac{\partial A_{1j}}{\partial \varepsilon_k} A_{2j} + A_{1j} \frac{\partial A_{2j}}{\partial \varepsilon_k}}{A_{2j}}, \tag{2.69}
\]

and the differentiations of involved equations are

\[
\frac{\partial B_{1j}}{\partial \varepsilon_k} = 2 \Re \left( e^{-i2\Delta_0} \frac{\partial r_{0j}^*}{\partial \varepsilon_k} \right) \left[ r_{aj} + \Re \left( r_{0j}^* e^{-i2\Delta_0} \right) \right]
\]

\[
+ 2 \Im \left( e^{-i2\Delta_0} \frac{\partial r_{0j}^*}{\partial \varepsilon_k} \right) \Im \left( r_{0j}^* e^{-i2\Delta_0} \right) \tag{2.70}
\]

\[
\frac{\partial B_{2j}}{\partial \varepsilon_k} = 2 r_{aj} \Re \left( e^{-i2\Delta_0} \frac{\partial r_{0j}^*}{\partial \varepsilon_k} \right) \left[ 1 + r_{aj} \Re \left( r_{0j}^* e^{-i2\Delta_0} \right) \right]
\]

\[
+ 2 r_{aj}^2 \Im \left( e^{-i2\Delta_0} \frac{\partial r_{0j}^*}{\partial \varepsilon_k} \right) \Im \left( r_{0j}^* e^{-i2\Delta_0} \right) \tag{2.70}
\]

\[
\frac{\partial r_{0j}^*}{\partial \varepsilon_k} = \frac{-n_n^2 - \sin^2 \theta_i}{\sqrt{(n + ik)^2 - \sin^2 \theta_i}} \frac{1}{\sqrt{n_n^2 - \sin^2 \theta_i} + \sqrt{(n + ik)^2 - \sin^2 \theta_i}} \tag{2.70}
\]
The Seraphin coefficients for unpolarized light can be calculated by using eqs. (2.54) and (2.55). Figures 2.10 and 2.11 show calculated Seraphin coefficients with and without film. The film thicknesses are 1, 10 and 100 nm for Fig. 2.10, and the dielectric constants of the films are 1.46 (proper for SiO₂), 1.8 and 2.2 for Fig. 2.11. The shape of Seraphin coefficient vertiginously
2.4 Relation between Reflectance and Dielectric Function

Figure 2.10: Calculated spectra of Seraphin coefficients of the structure without and with thin film, $\alpha$ and $\beta$ for layer stacked on a substrate. The layer thicknesses are 1, 10 and 100 nm.

Figure 2.11: Calculated spectra of Seraphin coefficients of the structure without and with thin film for layer stacked on a substrate. The refractive indices of the layers are 1.46, 1.8 and 2.2.

varies with thickness and dielectric constant of the film. This suggests that the shape of modulation spectrum strongly correlate with thickness and material of the film.
### 2.1 Photoreflectance Spectroscopy

#### b) 2 Layers

In the case of incidence through 2 layers as shown in Fig. 2.12, the reflectivity is expressed as a following equation [7],

$$ r^* = \frac{r_b A + B e^{-i2\Delta_b}}{A + Br_b e^{-i2\Delta_b}} = \frac{C_1}{C_2} \tag{2.74} $$

where

$$ A = 1 + r_a r_0^* e^{-i2\Delta_a} \tag{2.75} $$

$$ B = r_a + r_0^* e^{-i2\Delta_a} \tag{2.76} $$

$$ C_1 = r_b A + B e^{-i2\Delta_b} \tag{2.77} $$

$$ C_2 = A + Br_b e^{-i2\Delta_b} \tag{2.78} $$

$$ \Delta_a = \frac{2\pi d_a}{\lambda} n_a \cos \theta_a \tag{2.79} $$

$$ \Delta_b = \frac{2\pi d_b}{\lambda} n_b \cos \theta_b \tag{2.80} $$

The reflectivity $r_0^*$ and its differential for s- and p-polarized lights are shown as eqs. (2.62), (2.64) and (2.70)–(2.73), respectively. The reflectivity $r_a$ and $r_b$ for each polarized lights are expressed as following equations, respectively,

$$ r_{bs} = \frac{\cos \theta_1 - \sqrt{n_b^2 - \sin^2 \theta_1}}{\cos \theta_1 + \sqrt{n_b^2 - \sin^2 \theta_1}} \tag{2.86} $$
2.4 Relation between Reflectance and Dielectric Function

2.4.4 Complex Form of Reflectance

The relationship between reflectance and dielectric function shown as eq. (2.39) can be also expressed as complex form as shown below,

\[
\frac{\Delta R}{R} = \alpha \Delta \varepsilon_1 + \beta \Delta \varepsilon_2
\]

\[
= \Re \left[ \alpha \Delta \varepsilon_1 - (-1) \beta \Delta \varepsilon_2 + i \alpha \Delta \varepsilon_2 - i \beta \Delta \varepsilon_1 \right]
\]

\[
= \Re \left[ \alpha \left( \Delta \varepsilon_1 + i \Delta \varepsilon_2 \right) - i \beta \left( \Delta \varepsilon_1 + i \Delta \varepsilon_2 \right) \right]
\]

\[
= \Re \left[ \alpha - i \beta \right] \left( \Delta \varepsilon_1 + i \Delta \varepsilon_2 \right)
\]

\[
= \Re \left[ C_s \Delta \varepsilon^* \right], \quad (2.90)
\]
where $C_s = \alpha - i\beta$ and $\Delta \varepsilon^* = \Delta \varepsilon_1 + i\Delta \varepsilon_2$ are complex forms of Seraphin coefficient and dielectric function, respectively. Therefore, the reflectance difference is obtained by substituting eq. (2.28),

$$\frac{\Delta R}{R} = \Re \left[ C e^{i\theta} \left( E - E_g + i\Gamma \right)^{-n} \right].$$

(2.91)

where $n$ depends upon dimension of the critical point, is $\frac{7}{2}$ for 1D, 3 for 2D and $\frac{5}{2}$ for 3D. The spectrum for all energy region is expressed as summation of the spectrum for all critical points,

$$\frac{\Delta R}{R} = \Re \left[ \sum_j C_j e^{i\theta_j} \left( E - E_j + i\Gamma_j \right)^{-n_j} \right].$$

(2.92)

### 2.4.5 Dependence of PRS Spectrum on Thickness and Refractive Index of Film

Figures 2.14 and 2.15 show PRS spectra of SiO$_2$($n = 1.46$)/Si and high-refractive film($n = 2.2$)/Si structures calculated by using Seraphin coefficients discussed in § 2.4.3, respectively. The spectral shape varies for thick film ($> 100$ nm). Moreover, the refractive index affects the spectral shape. This drastic change of the spectral shape is caused by the interference effect in the film. On the other hand, the spectral intensity changes little with thickness and refractive index. This means that PRS spectral intensity is not affected by optical property of the transparent film.
2.4 Relation between Reflectance and Dielectric Function

Figure 2.14: Calculated PRS spectra of SiO$_2$($n = 1.46$)/Si structure. SiO$_2$ thicknesses are 10, 100, 200 and 300 nm.

Figure 2.15: Calculated PRS spectra of high-refractive film($n = 2.2$)/Si structure. The film thicknesses are 100, 200, 300 and 400 nm.
2.5 Spectral Intensity of Photoreflectance

2.5.1 Relation of PRS spectral intensity to Built-in Surface Potential

Under low electric field, the spectral intensity of PRS spectrum is proportional to square of electric field as shown in eq. (2.27) [23],

\[ \frac{\Delta R}{R} \propto E^2. \] (2.93)

For actual PRS measurement, there is the built-in potential by Fermi level pinning effect at Si surface, so that the electric field not equal to zero even without the external electric field. Measured PRS spectrum is difference between that under a certain field \( E \) and that under the built-in electric field \( E_0 \),

\[ \frac{\Delta R}{R} = \frac{\Delta R^E}{R} - \frac{\Delta R^{E_0}}{R} = kE^2 - kE_0^2 = k\Delta E^2, \] (2.94)

where \( k \) is constant which do not include the electric-field dependent term. Therefore, PRS spectrum is proportional to the difference between reflectances with and without electric field.

Figure 2.16 shows the energy band diagram near n-type Si surface with modulation light irradiation. \( \Psi_s \) and \( \Delta \Psi_s \) are the built-in surface potential and difference potential induced by photo-generated carrier.

From Poisson’s equation, the depletion width \( W \) and average electric field \( E(\Psi_s) \) is expressed as [10]

\[ W(\Psi_s) = \sqrt{\frac{2\epsilon_s \Psi_s}{qN_D}}, \] (2.95)

\[ E(\Psi_s) = \frac{\Psi_s}{W(\Psi_s)} = \sqrt{\frac{qN_D \Psi_s}{2\epsilon_s}}, \] (2.96)

Figure 2.16: Energy band diagram near n-type Si surface with light irradiation.
2.5 Spectral Intensity of Photoreflectance

Table 2.1: Variables for Si and Ar+ laser

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflectance ( R_0 )</td>
<td>0.39</td>
</tr>
<tr>
<td>Effective Richardson constant ( A^* )</td>
<td>120 A cm(^{-2}) K(^{-2})</td>
</tr>
<tr>
<td>Quantum efficiency ( \gamma )</td>
<td>0.58</td>
</tr>
</tbody>
</table>

where \( \varepsilon_s \) is the dielectric constant of Si. \( \Delta (E^2) \) in eq. (2.94) becomes

\[
\Delta (E^2) = E^2 (\Psi_s) - E^2 (\Psi_s - \Delta \Psi_s) = \frac{qN_D}{2\varepsilon_s} \Delta \Psi_s. \tag{2.97}
\]

Therefore,

\[
\frac{\Delta R}{R} \propto \Delta \Psi_s. \tag{2.98}
\]

where above relationship is true when the following inequality is satisfied,

\[
\Psi_s - E_c - E_F \gg q \Delta \Psi_s. \tag{2.99}
\]

Generally, this inequality is satisfied for almost of PRS measurement.

\( \Delta \Psi_s \) is caused by photo-voltage \( V_m \) by irradiation of modulation light, so \( \Delta \Psi_s = qV_m \). \( V_m \) is described by the equilibrium state of photo-generated carrier in the Schottky barrier. Neglecting recombination current in the depletion layer, we obtain a following equation [11].

\[
\frac{P_m \gamma (1 - R_0)}{\hbar \omega} = \frac{A^* T^2}{q} \exp \left( -\frac{\Psi_s}{kT} \right) \left[ \exp \left( \frac{qV_m}{nkT} \right) - 1 \right] \tag{2.100}
\]

where \( P_m \) is area density of modulation light power, \( A^* \) is the effective Richardson constant, \( \hbar \omega \) is photon energy of modulation light, \( \gamma \) and \( R_0 \) are quantum efficiency and reflectance of the sample at wavelength of modulation light, respectively, and \( n \) is the ideal factor. These variables for Si and Ar+ laser (wavelength \( = 488 \) nm) which has been used in this work are shown in Table 2.1. Solving eq. (2.100) for \( \Delta \Psi_s = qV_m \), we obtain,

\[
\Delta \Psi_s = nkT \ln \left[ \frac{qP_m \gamma (1 - R_0)}{A^* T^2 \hbar \omega} \exp \left( \frac{\Psi_s}{kT} \right) + 1 \right] \tag{2.101}
\]

where

\[
A = \frac{q\gamma (1 - R_0)}{A^* \hbar \omega}, \tag{2.102}
\]

is a constant. Therefore, from eqs. (2.98) and (2.101), PRS spectral intensity is expressed as a following equation,

\[
\frac{\Delta R}{R} = B \cdot \ln \left[ \frac{A \cdot P_m}{T^2} \exp \left( \frac{\Psi_s}{kT} \right) + 1 \right]. \tag{2.103}
\]

where \( B \) is a constant.
2.5.2 Effect of Thickness and Dielectric constant of Dielectric film on Si

For an ideal insulator/n-Si structure as shown in Fig. 2.17 (a), the potential \( V \) at surface of insulator film is expressed as a sum of the voltage (\( V_i \)) applied to an insulator film and that (\( V_s \)) applied to Si surface,

\[
V = V_i + V_s,
\]

where \( V_s = \frac{\Psi_s}{q} \). \( V_i \) is obtained by using the capacitance of insulator and the space charge \( Q_s \) induced at Si surface,

\[
V_i = \varepsilon d = \frac{|Q_s|d}{\varepsilon_i},
\]

where \( d \) and \( \varepsilon_i \) are thickness and dielectric constant of insulator film, respectively. \( Q_s \) is obtained by solving the Poisson equation at Si surface [12],

\[
|Q_s| = \sqrt{\frac{2\varepsilon_s kT}{qL_D} F (\Psi_s)},
\]

where, \( L_D \) is the Debye length expressed as \( L_D = \sqrt{\frac{\varepsilon_s kT}{q^2 n}} \). \( F (\Psi_s) \) is expressed as a function of Si surface potential \( \Psi_s \).

\[
F (\Psi_s) = \sqrt{\left(e^{\frac{\Psi_s}{kT}} + \frac{\Psi_s}{kT} - 1\right) + \frac{p}{n}\left(e^{\frac{\Psi_s}{kT}} - \frac{\Psi_s}{kT} - 1\right)}
\]

Thus, substituting these equations to eq. (2.104), we obtain relation between potential \( V \) at insulator surface and Si surface potential \( \Psi_s \),

\[
V = \frac{\Psi_s}{q} + \frac{d}{\varepsilon_i} \frac{\sqrt{2\varepsilon_s kT}}{qL_D} F (\Psi_s)
\]

PRS spectral intensity can be calculated by using \( \Psi_s \) obtained from eqs. (2.103) and (2.108). Figure 2.18 shows the dependence of PRS spectral intensity on the insulator thickness (\( d \)) calculated from eq. (2.103) by substituting \( \Psi_s \) obtained by numerical calculation using eq. (2.108),

Figure 2.17: Band diagrams of insulator/Si structure for (a) ideal case, and (b) case of existence of positive charge in insulator.
2.5 Spectral Intensity of Photorelectance

Figure 2.18: Peak intensities of calculated PRS spectra as a parameter of insulator thickness.

when $V = 1\ V$, $n = 10^{18}\ cm^{-3}$ and $T = 300\ K$. It is found that the PRS spectral intensity decreases with increasing insulator thickness. Moreover, the intensity for the high-$k$ ($\varepsilon_i > 3.9$) insulator is larger than that for SiO$_2$ ($\varepsilon_i = 3.9$).

In the case of the existence of the effective oxide charge density ($Q_o$) (per unit area) in the insulator (Fig. 2.17 (b)), the potential at insulator surface $V$ is transformed from ideal case (eq. (2.108)) as expressed by [12]

$$V = \frac{\Psi_s}{q} + \frac{d}{\varepsilon_i} \left[ \frac{\sqrt{2e_kT}}{qL_D} F (\Psi_s) + qQ_o \right].$$

The dependence of PRS spectral intensity on the positive oxide charge density ($Q_o$) calculated using eq. (2.103) by substituting $\Psi_s$ obtained by numerical calculation using eq. (2.109) is shown in Fig. 2.19. Si surface potential decreases and consequently PRS spectral intensity decreases, as shown in Fig. 2.19.
Figure 2.19: Dependence of PRS spectral intensity on positive oxide charge ($Q_o$) calculated using eqs. (2.109) and (2.103). Spectral intensity is normalized to equal 1 for ideal case ($Q_o = 0$).
2.6 Experiment of Photoreflectance

**Measurement condition**  Figure 2.20 shows a schematic diagram for PRS measurement. The surface potential of the sample is modulated with an Ar\(^+\) laser which has wavelength of 488 nm (Spectra-Physics Stabilite 2017) intermitted by a mechanical chopper (frequency: 100–200 Hz). Simultaneously, the sample is irradiated with a probe light from a Xe discharge lamp (Ushio UXL-500D) and reflected light from the sample is guided to the monochromator (Spex 1704). The light dispersed by the monochromator is detected by a photomultiplier (Hamamatsu R1508). A small change in reflectance (\(\Delta R\)) is measured by a lock-in amplifier (NF 5610B) referring to chopping frequency. The reflectance \(R\) is measured by digital multimeter (Advantest R6551). All PRS measurements are performed in air at room temperature. Detailed conditions of PRS measurement is shown in Table 2.2.

**Analysis of PRS spectrum**  Figure 2.21 shows an example of measured PRS spectrum of \(\text{Al}_2\text{O}_3/n-\text{Si}\) measured at room temperature. PRS spectrum is expressed by eq. (2.92). \(E'_0\) (3 dimension) and \(E_1\) (2 dimension) critical points exist in the spectral range 3–4 eV. So, measured data of PRS spectrum should be fitted by using following equation,

\[
\frac{\Delta R}{R} = \Re\left[C'_0 e^{i\theta'_0} (E - E'_0 + i\Gamma'_0)^{-5/2} + C_1 e^{i\theta_1} (E - E_1 + i\Gamma_1)^{-3}\right]. \tag{2.110}
\]

The solid line in Fig. 2.21 is fitted curve by using eq. (2.110). The fitted spectrum suits the measured data. The dashed line and dotted line are \(E'_0\) and \(E_1\) components of fitted spectrum, respectively. Fitted parameters of these components are shown in Table 2.3. It is found that \(E'_0\) and \(E_1\) almost equal to reported value [13] are obtained by this fitting. It is considered that the sample is modulated by not only photo-carrier generation (PRS) but also heating by irradiation of modulation laser light. The thermally modulated spectrum is expressed as first derivative of non-modulated spectrum [9], which has obviously different spectral shape. If the thermal modulation effect is not negligible, the measured data cannot be fitted by using eq. (2.110). Therefore, in this work, we consider that thermal effect by irradiation of modulation light is negligible, so eq. (2.110) is used for curve fitting of PRS spectrum.

**Measured region**  The penetration depth \(d_p\) of irradiated light is expressed as a following equation [1],

\[
d_p = \frac{\lambda}{4\pi k}, \tag{2.111}
\]

where \(\lambda\) is the wavelength of light and \(k\) is the extinction coefficient (imaginary part of complex refractive index), respectively. For Si, \(k\) is about 3 around \(E_1\) critical point, so \(d_p\) of the probe light becomes about 10 nm. Therefore, it is considered that the measured region by PRS is from surface to 10 nm.
Figure 2.20: Schematic diagram for PRS measurement.

Table 2.2: Conditions of PRS measurement.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probe light</td>
<td>Xe discharge lamp</td>
</tr>
<tr>
<td>Probe spot size</td>
<td>(~ 0.1 \text{ mm})</td>
</tr>
<tr>
<td>Modulation light</td>
<td>\text{Ar}^+ \text{ laser 488 nm}</td>
</tr>
<tr>
<td>Power of modulation light</td>
<td>0.2–1 W</td>
</tr>
<tr>
<td>Diameter of modulation light</td>
<td>1.4 mm</td>
</tr>
<tr>
<td>Wavelength region</td>
<td>330–400 nm</td>
</tr>
<tr>
<td>Chopping frequency</td>
<td>100–200 Hz</td>
</tr>
<tr>
<td>Incident angle of probe light</td>
<td>45°</td>
</tr>
<tr>
<td>Incident angle of modulation light</td>
<td>30°</td>
</tr>
<tr>
<td>Temperature</td>
<td>R. T.</td>
</tr>
</tbody>
</table>
2.6 Experiment of Photoreflectance

Figure 2.21: An example of PRS spectrum and fitted theoretical curve (solid line). Dashed and broken lines show spectra at $E_1$ and $E'_0$ critical points, respectively, composing of the fitted curve.

Table 2.3: The parameters of curve fitting in Fig. 2.21.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fitted value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C'_0$</td>
<td>$3.08 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\theta'_0$</td>
<td>$165^\circ$</td>
</tr>
<tr>
<td>$E'_0$</td>
<td>3.32 eV</td>
</tr>
<tr>
<td>$\Gamma'_0$</td>
<td>0.13 eV</td>
</tr>
<tr>
<td>$C_1$</td>
<td>$2.30 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\theta_1$</td>
<td>$41^\circ$</td>
</tr>
<tr>
<td>$E_1$</td>
<td>3.45 eV</td>
</tr>
<tr>
<td>$\Gamma_1$</td>
<td>0.13 eV</td>
</tr>
</tbody>
</table>
2.7 Summary

The theories of PRS have been described. The Seraphin coefficients, which show the relationship between reflectance and dielectric function, are calculated for dielectric film/Si structure. The spectral shape of PRS spectrum calculated by using Seraphin coefficients varies in the case of thick and high-refractive dielectric film/Si structure. On the other hand, PRS spectral intensity hardly depends on Seraphin coefficients.

PRS spectral intensity is expressed as a monotonically increasing function of Si surface potential. From calculation of space charge at Si surface of dielectric film/Si structure, it is found that PRS spectral intensity depends on thickness and dielectric constant of the film. Moreover, PRS spectral intensity is decreased by existence of positive charge in the film. It is considered that these properties of dielectric film can be investigated by using PRS.
Reference


Chapter 3

Characterization of SiO$_2$/Si Structure

3.1 Introduction

SiO$_2$ film has been used for the gate insulator for a long time because of its good characteristics. As described Chap. 1, alternative materials are examined instead of SiO$_2$ recently, it is still a basic and important material. In particular, the strained Si devices are expected for high-speed MOS-FET [1]. Hence, the necessity of evaluation techniques for determining the stress and strain has increased [2] curvature measurement [3, 4], electroreflectance [5] and Raman scattering [2] have already been proposed; however, these techniques have not yet been established as stress evaluation methods. We have attempted to apply PRS to monitor the stress induced at the SiO$_2$/Si interface [6]. The stress measurement was obtained by the empirical pseudopotential method [5] mentioned in Ref. [6]. In this chapter, characterization of SiO$_2$/Si structures by PRS is described. Firstly, the stress value is quantified by the shift of $E_1$ critical point obtained from PRS spectra, because it has been reported that $E_1$ critical point changes due to the strain induced at the Si/SiO$_2$ interface [7]. The stress was induced by using Si diaphragm structure. Secondly, the changes of stress and PRS spectral intensity with native oxide growth is monitored by PRS. As described in § 2.5.2, it is considered that SiO$_2$ thickness and the potential at SiO$_2$ surface can be characterized by PRS spectral intensity. Finally, PRS is applied to the stress between thermal oxidized SiO$_2$ and Si. Moreover, dependence of PRS spectral intensity on thickness of SiO$_2$ is discussed.

3.2 Measurement of Si Surface Stress by using Si Diaphragm

3.2.1 Sample Preparation

The n-Si (100) wafers (resistivity: $\sim 0.02$ $\Omega$ cm) were used for substrates. The Si diaphragm structure was fabricated to produce the strain at the Si surface by anisotropic etching in mixture of ethylenediamine pyrocatechol water (EPW). The mixing ratio of EPW solution was ethylenediamine(ml) :
Characterization of SiO$_2$/Si Structure

Figure 3.1: Cross-sectional view of the Si diaphragm structure prepared by preferential etching.

pyrocatechol(g) : water(ml) = 17 : 3 : 8. Covering the surface by thermal oxide, the Si substrate was etched from the back. Etching time and temperature of EPW solution were 10 h and 114°C, respectively. After etching, the thermal oxide on the surface was removed, and an ultrathin chemical oxide was newly grown by boiling with HNO$_3$ solution (60%, boiling point: 122°C) to enhance PRS spectral intensity.

The lateral dimensions of diaphragm were about 3×3 mm$^2$, and the thickness of the diaphragm was approximately 50 µm. The diaphragm was set and pressed from the back side by compressed N$_2$ gas. Cross sectional view of pressed diaphragm structure is shown in Fig. 3.1.

### 3.2.2 Strain estimation by elastic analysis

Prior to strain evaluation by PRS spectrum, the strain of the diaphragm was estimated by elastic analysis. The coordinate of the diaphragm is defined as horizontal center of the diaphragm becomes coordinate origin. The diaphragm is a regular tetragon, whose four sides are fixed. The side length is $2a$ and the thickness of the diaphragm is $h$. The bending rigidity of this diaphragm is given as

$$D \equiv \frac{E h^3}{12 (1 - \nu^2)},$$

where $E$ is Young’s modulus of Si and $\nu$ is Poisson’s ratio of Si. When a uniform pressure $P$ bends the diaphragm, the vertical displacement $w$ of the diaphragm is given as follows,

$$w(x, y) = \frac{\alpha}{12a^2D} \frac{P}{D} \left(x^2 - a^2\right)^2 \left(y^2 - a^2\right)^2,$$

where $\alpha$ is a constant ($\sim 0.383$).

The diaphragm deformation generates the bending stress $\sigma_x$ and horizontal strain $\epsilon_x$. When the central plane of the diaphragm is taken as the origin, the values of $\sigma_x$ and $\epsilon_x$ are given by the following equations:

$$\sigma_x (x, y, z) = \frac{E}{1 - \nu^2} \frac{z}{\rho_x (x, y)}$$

$$\epsilon_x (x, y, z) = \frac{z}{\rho_x (x, y)}$$
### 3.2 Measurement of Si Surface Stress by using Si Diaphragm

![Image](image1.png)  
Figure 3.2: Spacial distribution of calculated displacement $w$ of the diaphragm. The pressure $P$ is 100 kPa.

![Image](image2.png)  
Figure 3.3: Spacial distribution of calculated horizontal strain (x-component) $\epsilon_x$ at surface ($z = h/2$) of the diaphragm. The pressure $P$ is 100 kPa.

\[
\frac{1}{\rho_{x}(x,y)} = -\frac{\partial^2 w}{\partial x^2} (x,y), \quad (3.5)
\]

where $\epsilon_x > 0$ indicates a tensile strain and $\epsilon_x < 0$ indicates a compressive strain. From eqs. (3.3) and (3.4), the relationship between the stress and the strain is given by the following equation,

\[
\sigma_x = \frac{E}{1-\nu^2} \epsilon_x, \quad (3.6)
\]

The next equation is obtained by substituting $w(x,y)$ with eq. (3.2).

\[
\epsilon_x (x,y,z) = -\frac{2a}{9a^4} \frac{P}{D} \left(3x^2 - a^2\right) \left(y^2 - a^2\right)^2. \quad (3.7)
\]

Substituting $h/2$ for $z$, Si surface strain is obtained as follows,

\[
\epsilon_x (x,y) = -\frac{ah}{9a^4} \frac{P}{D} \left(3x^2 - a^2\right) \left(y^2 - a^2\right)^2. \quad (3.8)
\]

Figures 3.2 and 3.3 show the calculated distributions of displacement $w(x,y)$ and horizontal strain (x-component) at the diaphragm surface $\epsilon_x$ toward x-y position on the diaphragm, respectively. Where, $P = 100$ kPa, $E = 130$ GPa, $\nu = 0.28$ for Si (100) [8] are used for calculation.

The reliability of the estimation by the elastic analysis was confirmed by measuring the vertical displacement of the Si diaphragm by laser triangulation using an optical displacement gauge (as shown in Fig. 3.4). Figure 3.5 shows a comparison between the calculated displacement by elastic analysis and the directly measured one at points along x axis ($y = 0$). There is good agreement between the calculated and measured displacements. Hence, it is considered that the estimation by elastic analysis gives us reasonable results.

#### 3.2.3 Relation between PRS spectrum and Stress at Si Diaphragm Surface

The PRS spectra were measured for the Si diaphragm with and without N$_2$ gas pressing. Figure 3.6 shows the PRS spectra with and without gas pressing. It appears that N$_2$ gas pressing changes the
Characterization of SiO$_2$/Si Structure

Figure 3.4: Measurement of vertical displacement of Si diaphragm by using an optical displacement gauge.

Figure 3.5: Spacial distribution of calculated (dashed lines) and measured (open circles and squares) displacements along x-axis of the Si diaphragm.

PRS spectrum. $E_1$ critical point were obtained by curve fitting using eq. (2.110). The relationship between $E_1$ critical point and the N$_2$ gas pressure is shown in Fig. 3.7. The top axis of Fig. 3.7 is the surface stress obtained by using eqs. (3.6) and (3.8). It is found that $E_1$ critical point is proportional to the gas pressure and the surface stress $\sigma_x$.

As shown in Fig. 3.3, tensile strain is generated near the center of the diaphragm surface, while the compressive strain is generated near the fringe of the diaphragm. The lateral distribution of PRS spectrum was obtained by scanning the probe light beam along the x-axis on the x-y coordinate of the diaphragm. Near the center of the diaphragm, tensile strain is induced at diaphragm surface, as shown in Fig. 3.3. On the other hand, near the fringe of the diaphragm, compressive strain (negative value in Fig. 3.3) is induced. Figure 3.8 shows the relationship between the calculated strain and $E_1$ obtained from PRS spectra. The top axis of Fig. 3.8 is the surface stress obtained by using eq. (3.8). Figure 3.9 shows $E_1$ obtained from PRS spectra vs the surface stress obtained by combining Figs. 3.7 (open square) and 3.8 (open circle). $E_1$ critical point shows a good correlation with the surface stress. The dashed line in Fig. 3.9 shows the result of linear fitting expressed as a following equation.

$$E_1 = 3.45 - 0.001\sigma_x \, \text{[eV]}, \quad (3.9)$$

where the unit of $\sigma_x$ is MPa. $E_1$ critical point shifts to low energy side with tensile stress of Si surface.

As a result, Si surface stress $\sigma_x$ can be obtained from $E_1$ critical point by using a following
3.2 Measurement of Si Surface Stress by using Si Diaphragm

Figure 3.6: Measured PRS spectra with (solid line) and without (dashed line) stress application induced by N₂ gas pressing.

Figure 3.7: E₁, transition energy of critical point obtained from PRS spectra as a function of N₂ gas pressure. Interpolated curve is shown with dashed line.

Figure 3.8: E₁, transition energy of critical point and stress obtained from lateral distribution as a function of calculated strain.

Figure 3.9: E₁, transition energy of critical point vs. the surface stress of the diaphragm.
equation,

$$\sigma_x = a(E_1(0) - E_1(\sigma_x)), \quad (3.10)$$

where $a = 1 \times 10^{-9}$ eV/Pa. $E_1(0)$ is $E_1$ critical point in the case of no stress in Si. It is well known that Si surface is given large tensile stress by Si oxide grown on that [9]. We should note that there is stress in the diaphragm even without N$_2$ gas pressing because of existing the oxide to PRS spectra measurable. So, $E_1(0)$ is not equal to 3.45 eV. $E_1(0)$ is obtained from PRS measurement of native oxidation of Si, as described in a follow section.
3.3 Monitoring of Native Oxide Growth

3.3.1 Experimental Procedures

After cleaning by RCA method, Si (100) substrates (n-type or p-type, resistivity: \(\sim 0.02\ \Omega\ \text{cm}\)) were dipped into buffered HF (NH\(_4\)HF\(_2\) 20\%) to remove the surface oxide. Then they were exposed to air for about 90 d to grow native oxide. X-ray photoelectron spectroscopy (XPS) measurement was carried out for determination of native oxide thickness. Si 2p spectra were measured by XPS instruments (Shimadzu-Kratos Axis-Hsi2). The X-ray source with Mg K\(\alpha\) radiation was used without a monochromator. SiO\(_2\) thickness \(d_{\text{ox}}\) were determined from ratio of chemically-shifted integrated intensity \(I_{\text{SiO}_2}\) to not-shifted integrated intensity \(I_{\text{Si}}\) of Si 2p peak, using by following equation [10],

\[
d_{\text{ox}} = \lambda_{\text{SiO}_2} \cos \theta \ln \left( k \frac{I_{\text{SiO}_2}}{I_{\text{Si}}} + 1 \right),
\]

where \(k = 2.086\) is a constant, \(\lambda_{\text{SiO}_2} = 2.5\ \text{nm}\) is the escape depth of photoelectron in SiO\(_2\), and \(\theta\) is the escape angle of photoelectron.

3.3.2 PRS Spectral Intensity with Native Oxide Growth

Figure 3.10 shows PRS spectra of naturally oxidized n-Si as a parameter of the exposure time. PRS spectral intensity increases with increasing the exposure time. The dependence of XPS Si 2p spectrum intensity on the exposure time is shown Fig. 3.11. It is found that chemical-shifted peak intensity (from the Si-O bond) increases with increasing the exposure time. Thus, native oxide growth progresses continually with exposure to air.

Figure 3.12 shows PRS spectral intensity and native oxide thickness calculated from eq. (3.11) as a function of the exposure time. Assuming that the oxide growth follows Deal-Groove model, the oxide thickness is expressed a following equation in the case of a long time oxidation [9],

\[
d_{\text{ox}}^2 \approx Bt,
\]

where \(B\) is parabolic rate constant. The dot-dashed curve in Fig. 3.12 is the curve fitted to measured oxide thickness by eq. (3.12). The rate constant \(B\) is determined 0.000171 nm\(^2\)/h by curve fitting. Figure 3.13 shows PRS spectral intensity vs native oxide thickness calculated from eq. (3.12). PRS spectral intensity is approximately proportional to native oxide thickness. Assuming that the potential at native oxide surface is constant, PRS spectral intensity must decrease with increasing the oxide thickness, as shown in Fig. 2.18. Therefore, this result means that the potential at native oxide surface increases with native oxidation.

On the other hand, for p-type Si, PRS spectral intensity decreases with increasing the exposure time as shown in Fig. 3.14. PRS spectral intensity is expressed as a function of downward
Figure 3.10: Dependence of PRS spectra on the exposure time in air atmosphere.

Figure 3.11: Dependence of XPS Si $2p$ spectra on the exposure time.

Figure 3.12: PRS spectral intensity (open square) and native oxide thickness (closed circle) as a function of the exposure time.

Figure 3.13: PRS spectral intensity vs. native oxide thickness.
3.3 Monitoring of Native Oxide Growth

Figure 3.14: PRS spectral intensity as a function of the exposure time for p-type Si.

Figure 3.15: Energy band diagram for insulator/p-Si structure.

band bending in the energy band diagram for p-Si, as shown in Fig. 3.15 (cf. Fig. 2.17 for n-Si). Thus, when the potential $V$ at oxide surface changes from downward to upward in band diagram corresponding to conduction type of Si (it means that surface charge at oxide surface changes from positive to negative), PRS spectral intensity for n-Si increases and that for p-Si decreases, respectively.

We can consider a following model from these results. Si surface is positively charged by hydrogen-termination just after HF treatment. Hydrogen-termination decreases as Si surface is naturally oxidized. The SiO$_2$ surface is negatively charged in air [11] because of adsorbed hydroxide ions [12].

3.3.3 Increase of Tensile Stress by Native Oxide Growth

PRS spectra normalized by peak intensity of them are shown in Fig. 3.16 (same spectra in Fig. 3.10). PRS spectrum shifts to low energy side with increasing the exposure time. The shift of $E_1$ critical point obtained by curve fitting of PRS spectrum is shown in Fig. 3.17. $E_1$ critical point linearly changes toward native oxide thickness.

The stress is usually sum of thermal stress and intrinsic stress [2]. The thermal stress is generated when the sample is cooled after oxide growth, and originates from difference of thermal expansion coefficient between SiO$_2$ and Si. The intrinsic stress is due to the molar volume mismatch between the Si substrate and the oxidized SiO$_2$ film, as shown in Fig. 3.18. In this temperatures case, oxidation and PRS measurement temperatures are the same, room temperature, hence thermal stress is almost zero and the stress is only the intrinsic stress.

The dashed line in Fig. 3.17 shows a linear fitting result. $y$-intercept of this line is $E_1 \sim 3.59$ eV. It is considered that the surface stress is zero at $d_{ox} = 0$ so that $E_1(0)$ in eq. (3.10) is
3. Characterization of SiO$_2$/Si Structure

Figure 3.16: Dependence of shift of PRS spectra on the exposure time of Si in atmosphere.

Figure 3.17: Oxide thickness dependences of $E_1$, the transition energy at $E_1$ critical point obtained by curve fitting of PRS spectrum and interface stress.

Figure 3.18: Model illustration of appearance of tensile stress at Si interface induced by oxide growth.
3.3 Monitoring of Native Oxide Growth

3.59 eV. The right axis of Fig. 3.17 shows stress calculated from eq. (3.10). It is found that the Si surface stress reaches 200 MPa when native oxide grows to 0.3 nm.
3.4 Characterization of Thermal Oxidation

3.4.1 Experimental Procedure

The n-Si (100) wafers (∼ 0.02 Ω cm) were cleaned by RCA method and treated by buffered HF to remove of the native oxide. The growth of SiO₂ thin film was carried out in a dry O₂ atmosphere. The oxide thickness was measured by the ellipsometer (Mizojiri DVA-36W-UV) or XPS. Figure 3.19 shows comparison of the oxide thickness measured by XPS with that measured by ellipsometry. Both thicknesses well agree in the range 2–5 nm, however, they do not agree in further range. Thickness measurement by XPS is valid in $d_{ox} < 3\lambda_{ox} = 7.5$ nm [13]. Thus, we use SiO₂ thickness value measured by XPS in the range less than 5 nm or by ellipsometry in above range.

3.4.2 Stress at Interface between Si and Thermal Oxide

Large strain arises on the surface because of the lattice mismatch between Si and SiO₂ as well as the case of native oxide growth. Si receives tensile strain and SiO₂ receives compressive strain. According to previous reports [2–5], the stress decreases as the growth temperature of the oxide increases. PRS spectra were measured for samples oxidized at various growth temperatures for 30 min. Figure 3.20 shows PRS spectra for these samples. The spectra are normalized by peak intensity of them. The spectrum of the lower oxidation samples is located at a lower energy side than that of the higher oxidation sample. Figure 3.21 shows the relationship between the growth temperature of the oxide and $E_1$ critical point obtained by curve fitting of PRS spectra. $E_1$ increases with increasing growth temperature. The stress calculated from $E_1$ by using eq. (3.10) is as shown on the right-hand-side y-axis in Fig. 3.21. The stress decreases with increasing growth temperature. These results agree well with tendencies of the previous reports [2–5]. The oxide thickness is 10–1000 nm, as mentioned in Refs. [2–4], however, 1–5 nm oxide thickness was used in this experiment. The stress value in the previous reports (∼ 300 MPa at 700°C) is larger than our value (∼ 100 MPa at 700°C). Hence, we considered that the stress is lower than that mentioned in previous reports.

Generally, the Raman spectroscopy is utilized for characterization of lattice strain [14]. Figure 3.22 shows Raman spectra (Renishaw Ramascope1000) of SiO₂/Si structures. The SiO₂ thicknesses are 0.7, 5, 6, 10 nm, respectively. The Raman peak shift caused by lattice strain cannot be observed in Fig. 3.22. The Ar ion laser (514.5 nm) was used for exciting light source of these raman measurement. Using eq. (2.111), the penetration depth at 514.5 nm is about 500 nm. Therefore, raman peak includes characteristics at not only Si surface but also inside to 500 nm. It is considered that the intrinsic stress caused by the molar volume mismatch between the Si substrate and the SiO₂ film localizes near Si surface. Moreover, the Raman shift is 3–8 cm⁻¹/GPa (for zinc
3.4 Characterization of Thermal Oxidation

Figure 3.19: Relation between oxide thicknesses estimated by XPS and that measured by ellipsometry.

Figure 3.20: PRS spectra for samples oxidized at various temperatures. Peak intensity are normalized with positive peak value.
**3 Characterization of SiO$_2$/Si Structure**

![Graph](image1)

Figure 3.21: $E_1$ transition energy at critical point and corresponding stress as a function of oxide growth temperature.

![Graph](image2)

Figure 3.22: Raman peaks at 520 cm$^{-1}$ of the SiO$_2$/Si structures. The SiO$_2$ thicknesses are 0.7, 5, 6, 10 nm, respectively.

blende structure, by hydrostatic pressure). Very high spectral resolution ($\sim 0.01$ cm$^{-1}$) need to measure the stress of 10 MPa. It is considered that PRS is better for stress measurement near Si surface and smaller order ($\sim 10$ MPa) than Raman spectroscopy.

### 3.4.3 Dependence of PRS Spectral Intensity on SiO$_2$ Thickness

To measure the dependence of PRS spectral intensity on SiO$_2$ thickness, the thermally oxidized SiO$_2$ films which have various thicknesses were prepared by changing the oxidation time or etching time by dilute HF (0.1%). Figure 3.23 shows PRS spectral intensity as a function of thermal oxide thickness. PRS spectral intensity decreases with increasing thickness of 3 nm and above. This dependence agrees with that in Fig. 2.18. It is considered that the potential at SiO$_2$ (> 3 nm) surface becomes a constant value. On the other hand, the spectral intensity increases with increasing thickness less than 3 nm. This dependence can be explained similarly to § 3.3.2. Namely, SiO$_2$ surface charge gradually varies from positive to negative with increasing SiO$_2$ thickness (< 3 nm).

### 3.5 Summary

The SiO$_2$/Si structure has been characterized by PRS. Si diaphragm structure was prepared by anisotropic etching to give stress to Si surface. $E_1$ critical point obtained from curve fitting of PRS spectrum is linearly changed by Si surface stress given by pressing Si diaphragm. It is found that relationship between $E_1$ and Si surface stress is obtained by using elastic analysis of diaphragm so that Si surface stress can be estimated from the PRS spectrum.
Figure 3.23: PRS spectral intensity as a function of SiO$_2$ thickness. Open squares show samples prepared by various oxidation time, closed diamonds show samples prepared by HF etching.

PRS spectral intensity increases with native oxide growth. This means that surface charge at native oxide varies from the positive value to the negative with growth. Moreover, $E_1$ critical point obtained from PRS spectrum linearly decreases with native oxide thickness. It is considered that the tensile stress at Si surface increases with oxide growth because of molar volume mismatch between Si substrate and SiO$_2$ film.

Si surface stress by thermally-oxidation decreases with increase of oxidation temperature. Estimated tensile stress is about 150 MPa for 600°C growth and about 90 MPa for 900°C growth. The dependence of PRS spectral intensity on SiO$_2$ thickness has been measured. PRS spectral intensity decreases with increasing thickness of 3 nm and above. On the other hand, it increases with increasing thickness of less than 3 nm. It is considered that PRS spectral intensity is inseparably connected to the charge state at SiO$_2$ surface.
Reference


Chapter 4

Characterization of High-\(k\)/Si Structures

4.1 Introduction

As mentioned in Chap. 1, high-\(k\) films have various difficulty compared with SiO\(_2\). In particular, growth of the interfacial layer between film and substrate and large fixed charges in film affect electric characteristics of FET fabricated using high-\(k\)/Si structure. The interfacial layer decreases total dielectric constant of the film so that capacitance of the film closes to SiO\(_2\). The flat band shift is caused by fixed charges. Their effects emerge as change of Si surface potential. PRS spectral intensity is a function of Si surface potential, as shown in § 2.5. So, it is considered that their affects can be characterized by PRS spectral intensity.

In this chapter, various high-\(k\) thin films/Si structures are characterized by PRS. The excimer laser irradiation effect is employed to confirm the relation between amount of defects in high-\(k\) film and PRS spectral intensity. It is already reported that defects in SiO\(_2\) film is increased by laser irradiation [1]. Then deposition conditions and rapid thermal annealing (RTA) conditions of HfO\(_2\), PrO\(_x\) and other materials films are characterized by using PRS. HfO\(_2\) is mainstream of the material for gate oxides in recently [2, 3]. PrO\(_x\) (because the prepared film includes Pr\(_2\)O\(_3\) and Pr\(_6\)O\(_{11}\) phase [5]) has been one of high-\(k\) film of lanthanoid oxide candidates. Lanthanoid oxides have high dielectric constant (20–30), so they have attracted attention as next-generation high-\(k\) materials [4].
4.2 Sample Preparation

4.2.1 Pulsed Laser Deposition Method

After RCA cleanings and buffered HF (NH₄HF₂ 20%) treatment, high-\(k\) thin films were deposited on Si substrate by using pulsed laser deposition (PLD) method. PLD has following features [5];

- wide range of ambient gas pressure
- carbon-free
- no plasma damage

The schematic diagram of PLD equipment is shown in Fig. 4.1. Samples were set in high-vacuum chamber, then ArF excimer laser beam (Lambda Physik LPX 100; wavelength: 193 nm) was applied to the ceramic targets and ablated particles were deposited on Si surface. The detailed condition of PLD is shown in Table 4.1.

For electric characterization, Al electrodes were deposited by vacuum evaporation (Ulvac EBH-6) on HfO₂/Si. The base vacuum chamber pressure is about \(2 \times 10^{-6}\) Torr. The size of electrode is about 0.15 mmφ.

4.2.2 Metal Organic Decomposition Method

Some high-\(k\) films were also deposited by metal-organic decomposition (MOD) method. This method allows a simple preparation without vacuum process and a film deposited uniformly. After organic cleanings and HF treatment, a precursor solution (Kojundo SK-AL04, SYM-ZR04 and SYM-LA01) was spin-coated on Si substrate. Then samples were dried in air and annealed in O₂ atmosphere. Detail of MOD process is shown in Fig. 4.2. The materials are ZrO₂, Al₂O₃ and La₂O₃.

4.2.3 RTA Treatment

The rapid thermal annealing (RTA) is an annealing treatment using the infrared heating equipment (Nihon-tokusyukikai VF-11-461F). Figure 4.3 shows the sample-temperature control process for RTA. The sample is rapidly heated-up by irradiation of an infrared lamp. The rate of heat-up is about 50°C/sec. Then the sample temperature is held constant for holding time. The furnace is cooled by coolant water after holding temperature. The atmospheres of RTA treatment are N₂, O₂ and H₂(5%)/N₂ (known as a forming gas). The flow rate of gas is 1 l/min.
4.2 Sample Preparation

Figure 4.1: Schematic diagram of PLD apparatus.

Table 4.1: Deposition conditions of PLD.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintered target</td>
<td>HfO$_2$, Pr$<em>6$O$</em>{11}$ ceramics</td>
</tr>
<tr>
<td>Substrate</td>
<td>n-type Si(100) (0.01–0.02 $\Omega$ cm) for PRS measurement</td>
</tr>
<tr>
<td></td>
<td>n-type Si(100) (1000–2000 $\Omega$ cm) for ESR measurement</td>
</tr>
<tr>
<td></td>
<td>p-type Si(100) (0.7–10 $\Omega$ cm) for electric measurement</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>R. T.–600°C</td>
</tr>
<tr>
<td>Gas</td>
<td>O$_2$, N$_2$</td>
</tr>
<tr>
<td>Pressure</td>
<td>~ 0.02 Torr</td>
</tr>
<tr>
<td>Laser</td>
<td>ArF excimer (193 nm)</td>
</tr>
<tr>
<td>Repetition frequency</td>
<td>1.0 Hz</td>
</tr>
<tr>
<td>Shot energy</td>
<td>90 mJ/cm$^2$/shot</td>
</tr>
<tr>
<td>Target-substrate distance</td>
<td>40–60 mm</td>
</tr>
</tbody>
</table>
Figure 4.2: Flow chart of MOD process.

Figure 4.3: Control process of the sample temperature for RTA.
4.3 Excimer Laser Irradiation Effect

The samples were irradiated with ArF excimer laser light in air at room temperature. Figure 4.4 shows the electron spin resonance (ESR) spectra of HfO$_2$/Si structure with and without ArF laser irradiation. The peak around $g \approx 2.003$ increases with the laser irradiation. It is considered that this peak arises from oxygen vacancy in the HfO$_2$ film, not from interface defects, since it is independent of the direction of the magnetic field [6]. From the ESR results (Fig. 4.4), the laser irradiation generated unpaired electrons induced by oxygen vacancy in the HfO$_2$ film. It is considered that the dangling bonds of Hf atoms are generated by the laser irradiation.

The $C$-$V$ curves of the Al/HfO$_2$/Si structure with and without the laser irradiation are shown in Fig. 4.5. The $C$-$V$ curves are normalized by accumulation capacitance of them. The $C$-$V$ curves shift to the negative voltage direction. This result implies that the positive fixed charge in the HfO$_2$ film increases with the laser irradiation. From ESR and $C$-$V$ measurement, it should be considered that the HfO$_2$ film becomes positively charged as a result of these dangling bonds.

Figure 4.6 shows PRS spectral intensity as a function of the number of laser shots. The intensity is normalized by the intensity of the as-deposited sample. The spectral intensity decreases with increasing number of laser shots. It is unlikely that the surface potential at HfO$_2$ film is changed by laser irradiation, so it is considered that PRS spectral intensity reflects amount of positive charge in the film.
4 Characterization of High-κ/Si Structures

Figure 4.4: ESR spectra of HfO₂/Si structure without and with ArF laser irradiation.

Figure 4.5: C-V curve of Al/HfO₂/Si with and without ArF laser irradiation.
Figure 4.6: PRS spectral intensity as a function of number of laser shots normalized by PRS intensity of as-deposited sample.
4.4 HfO$_2$/Si Structure

4.4.1 Deposition Condition Dependence

HfO$_2$ thin films were deposited on Si substrate by PLD. The dependences on deposition atmosphere and on deposition temperature have been investigated.

Figure 4.7 shows the PRS spectra of HfO$_2$/Si structures deposited in O$_2$, N$_2$ and a mixture of these gases (O$_2$ : N$_2$ = 2 : 1) at 400°C. PRS spectral intensity depends on the deposition atmosphere. The positive fixed charges per unit area in the HfO$_2$ film calculated from a flat band voltage shift ($\Delta V_{FB}$) of C-V curves and PRS spectral intensities are shown in Fig. 4.8. The positive charge in the HfO$_2$ film deposited in N$_2$ is larger than that in the HfO$_2$ film deposited in the other atmospheres. This larger positive charge is assumed to be caused by oxygen vacancy because HfO$_2$ film is deposited in reduced atmosphere. On the other hand, PRS spectral intensity of HfO$_2$/Si deposited in N$_2$ is smaller than that of HfO$_2$/Si deposited in the other atmospheres. PRS spectral intensity decreases with increasing positive charge, as discussed in § 4.3. Thus, the relationship between deposition atmosphere and positive charge in the film can be investigated by PRS.

The PRS spectral intensity of HfO$_2$/Si deposited in O$_2$ is smaller than that of HfO$_2$/Si deposited in the mixture gas in spite of smaller charge density of the former. Assuming that the potential at HfO$_2$ surface (V) is constant, PRS spectral intensity decreases with decreasing the dielectric constant or increasing film thickness for HfO$_2$ film, as shown in Fig. 2.18. Figure 4.9 shows the cross-sectional TEM images of HfO$_2$/Si deposited in (a) O$_2$ and (b) N$_2$ at 400°C. The interfacial layer growth is observed in the TEM image of HfO$_2$ deposited in O$_2$ (Fig. 4.9 (a)). Similar results are obtained by measurement of the XPS spectrum of Si 2p. The interfacial layer includes Si oxide so that it has lower dielectric constant than that of HfO$_2$. From these results, it is considered that a small PRS spectral intensity is caused by lower dielectric constant because of the interfacial layer growth.

Figure 4.10 shows dependence of PRS spectrum on HfO$_2$ deposition temperature. PRS spectral intensity increases with increasing deposition temperature. C-V characteristics of Al/HfO$_2$/Si deposited at temperatures 100, 200, 300 and 400°C are shown in Fig. 4.11. Although the flat band voltage shift scarcely changes with deposition atmosphere, the accumulation capacitance (the maximum capacitance of C-V curve) increases with increasing temperature. Figure 4.12 shows PRS spectral intensity and the maximum of C-V curve as a function of HfO$_2$ deposition temperature. It is found that there is correlationship between PRS spectral intensity and the maximum capacitance. The accumulation capacitance almost equal to capacitance of HfO$_2$ film. Assuming thickness of HfO$_2$ film is independent on deposition temperature, it should be considered that dielectric constant of HfO$_2$ film increases with deposition temperature. PRS intensity also increases with dielectric constant of HfO$_2$ film, as shown in Fig. 2.18. Figure 4.13 shows Si surface stress in
Figure 4.7: PRS spectra of HfO$_x$/Si deposited in O$_2$, N$_2$ and a mixture (O$_2$ : N$_2$ = 2 : 1) gas.

Figure 4.8: Fixed oxide charges and PRS spectral intensities of HfO$_2$/Si deposited in O$_2$, N$_2$ and N$_2$/O$_2$ mixture gas.

Figure 4.9: Cross-sectional TEM images of HfO$_2$/Si deposited in (a) O$_2$ and (b) N$_2$ at 400°C.
### 4.4 Characterization of High-k/Si Structures

**Figure 4.10:** Dependence of PRS spectrum on HfO₂ deposition temperature.

**Figure 4.11:** Dependence of the C-V characteristic on HfO₂ deposition temperature.

**Figure 4.12:** PRS spectral intensity and maximum capacitance of C-V curve as a function of HfO₂ deposition temperature.

**Figure 4.13:** Si surface stress obtained from $E_1$ critical point of PRS spectra as a function of HfO₂ deposition temperature.

HfO₂/Si obtained by PRS curve fitting as a function of deposition substrate temperature. Dashed line in Fig. 4.13 shows the tensile stress value induced native oxide (0.3 nm) shown in Fig. 3.17. Although the tensile stress at Si surface slightly increases with increasing substrate temperature, it do not reach to the stress at interface between native oxide and Si. This result means that the interfacial layer growth is hardly observed for deposition at up to 400°C.

#### 4.4.2 RTA Condition Dependence

PRS was utilized for the characterization of RTA in N₂, O₂ and a forming gas. The holding time for RTA was 0 sec.

The dependences of fixed charge density obtained from C-V curves and PRS spectral intensity
on RTA temperature in N$_2$ atmosphere are shown in Fig. 4.14. The PRS spectral intensity of the sample annealed at 600°C is larger than that of that annealed at 500°C for RTA in N$_2$. As discussed previously, PRS intensity decreases with increasing positive charge in the film. Therefore, it is suggested that the reduction in the number of positively charged defects in HfO$_2$ by RTA is found by PRS.

The spectral intensity rapidly decreases at 700°C and above for RTA in N$_2$. Figure 4.15 shows the XPS spectra of the Si 2$p$ of HfO$_2$/Si structure treated by RTA in N$_2$. The signal from substrate at 99.4 eV [8] was used for the binding energy reference. The chemically-shifted peak (SiO$_2$: 103.4 eV [8]) of Si 2$p$ rapidly increases at high temperatures. This result means that an interfacial layer (including Hf-silicate and SiO$_2$) grows by RTA at high temperatures. Similar results are obtained by TEM image. The decrease in PRS spectral intensity corresponds to an interfacial layer growth found by XPS measurement. It is considered that the spectral intensity decreases with decreasing dielectric constant of HfO$_2$, as shown in Fig. 2.18. It is suggested by these PRS results that suitable temperature for RTA in N$_2$ atmosphere of HfO$_2$/Si structure is 600°C.

Figure 4.16 shows the PRS spectral intensity of HfO$_2$/Si as a function of temperature of RTA in O$_2$ atmosphere. PRS spectral intensity has a similar temperature dependence to the case of RTA in N$_2$. Figure 4.17 shows XPS spectra of HfO$_2$/Si structure treated by RTA in O$_2$ atmosphere. The SiO$_2$ peak of Si 2$p$ rapidly increases at high temperatures as well as N$_2$ RTA. The interfacial growth for O$_2$ RTA is larger than that for N$_2$ RTA. Therefore, the positive charge in HfO$_2$ film decreases by RTA in O$_2$ at up to 600°C and the interfacial layer growth occurs by RTA in O$_2$ above 700°C, so that it is considered that the suitable temperature for RTA in O$_2$ atmosphere of HfO$_2$/Si structure is also 600°C.

Figure 4.18 shows the PRS spectral intensity of HfO$_2$/Si as a function of temperature of RTA in the forming gas atmosphere. Although PRS spectral intensity has a similar temperature depen-
4 Characterization of High-$k$/Si Structures

Figure 4.15: XPS Si 2$p$ spectra of HfO$_2$/Si structure treated at 500, 600 and 800$^\circ$C by RTA in N$_2$.

Figure 4.16: PRS spectral intensity as a function of temperature of RTA in O$_2$ atmosphere.
4.4 HfO$_2$/Si Structure

![XPS Si 2p spectra of HfO$_2$/Si structure treated at 500, 600, 700 and 800°C by RTA in O$_2$ atmosphere.](image)

Figure 4.17: XPS Si 2p spectra of HfO$_2$/Si structure treated at 500, 600, 700 and 800°C by RTA in O$_2$ atmosphere.

dence to the case of RTA in N$_2$ and O$_2$, the increase in PRS intensity occurs at up to 500°C for RTA in the forming gas. Figure 4.19 shows XPS spectra of HfO$_2$/Si structure treated by RTA in the forming gas atmosphere. The chemically-shifted peak of Si 2p rapidly increases at 600°C and above. The increase in the area of an interfacial layer for forming gas RTA occurs at a lower temperature than those for the other atmospheres. Moreover, the chemically-shifted peak locates at a lower binding energy than SiO$_2$. This means that the composition of the interfacial layer grown by forming gas RTA is more silicate-like than that grown by O$_2$ and N$_2$ RTA. The forming gas is generally used for sintering of electrodes because of reducing behavior of H$_2$. So, it is considered that Hf oxide is reduced and then Hf-Si-O bond is formed by forming gas annealing. Anyhow, we can determine the suitable temperature for forming gas RTA 500°C by PRS spectral intensity.
4 Characterization of High-k/Si Structures

Figure 4.18: PRS spectral intensity as a function of temperature of RTA in the forming gas atmosphere.

Figure 4.19: XPS Si 2p spectra of HfO₂/Si structure treated at 500, 600 and 800°C by RTA in the forming gas atmosphere.
4.5 PrO$_x$/Si Structure

4.5.1 Deposition Condition Dependence

Figure 4.20 shows PRS spectra of PrO$_x$/Si structure deposited in O$_2$ atmosphere (0.2 Torr) and high-vacuum ($1 \times 10^{-7}$ Torr). PRS spectral intensity of the sample deposited in O$_2$ atmosphere is larger than that deposited in high-vacuum. It is considered that PrO$_x$ deposited in O$_2$ has less oxygen vacancy so that PRS spectral intensity is enhanced by less positive charges in the film. It is also found that PrO$_x$ deposited in high-vacuum has large positive charges from flat band voltage shift of C-V curve [5].

Figure 4.21 shows PRS spectra of PrO$_x$/Si structure deposited at various substrate temperatures. PRS spectral intensity increases with deposition temperature. It is considered that PrO$_x$ film deposited at higher temperature has higher dielectric constant because of higher film density observed by grazing incidence X-ray reflectometry (GIXR) [5]. Moreover, PRS spectrum seems to shift to low energy side for the sample deposited at high substrate temperature. Figure 4.22 shows Si surface stress in PrO$_x$/Si obtained by PRS curve fitting as a function of deposition substrate temperature. The tensile stress at Si surface significantly increases with increasing substrate temperature in sharply contrast to HfO$_2$ (Fig. 4.13). Dashed line in Fig. 4.22 shows the tensile stress value induced native oxide (0.3 nm) shown in Fig. 3.17. The stress value of PrO$_x$/Si deposited at higher temperature comes closer in this value. This result means that the interface between PrO$_x$ and Si substrate becomes like SiO$_2$/Si. Figure 4.23 shows TEM image of PrO$_x$/Si structure deposited at 400$^\circ$C. The interfacial layer growth is observed. From these results, it is considered that the interfacial layer which is like SiO$_2$ grows in the case of deposition at high substrate temperature, as shown in Fig. 4.24.

4.5.2 RTA Condition Dependence

PrO$_x$/Si structure deposited by PLD in O$_2$ atmosphere is treated by RTA. The holding time of RTA is for 1 min. The temperature and atmosphere of RTA are 400–800$^\circ$C and O$_2$ gas, respectively.

Figure 4.25 shows dependence of PRS spectra of PrO$_x$/Si on RTA temperature. PRS spectral intensity is rapidly decreased by RTA above 600$^\circ$C. XPS Si 2p spectra of these samples are shown in Fig. 4.26. The chemically-shifted peak corresponding to Si oxide is increased by RTA above 600$^\circ$. It is considered that the interfacial layer including SiO$_2$ and silicate is significantly grown by high-temperature RTA. The interfacial layer has lower dielectric constant than PrO$_x$ film so that effective dielectric constant of total film decreases. If dielectric constant decreases, PRS spectral intensity decreases as shown in Fig. 2.18. Figure 4.27 shows Si surface stress obtained from PRS spectra as a function of RTA temperature. Si surface stress is increased by RTA. Moreover, the stress induced by RTA at 600$^\circ$C becomes like that of native SiO$_2$/Si. This result fortifies the
Characterization of High-$k$/Si Structures

Figure 4.20: PRS spectra of PrO$_x$/Si structure deposited in O$_2$ atmosphere and high-vacuum.

Figure 4.21: PRS spectra of PrO$_x$/Si structure deposited at room temperature, 200°C, 400°C and 600°C.

Figure 4.22: Si surface stress in PrO$_x$/Si obtained by PRS curve fitting as a function of deposition substrate temperature.
4.5 PrOx/Si Structure

Figure 4.23: Cross-sectional TEM image of PrOx/Si structure.

Figure 4.24: Model illustration of PrOx/Si structure deposited (a) at low temperature and (b) at high temperature.

Figure 4.25: Dependence of PRS spectra of PrOx/Si on RTA temperature.
interfacial layer growth by RTA at high temperature.
4.6 Other High-κ Materials

ZrO₂, Al₂O₃ and La₂O₃ were characterized except HfO₂ and PrOₓ as described above. Their films were deposited on Si substrate by MOD. Figure 4.28 shows the dependence of PRS spectra on ZrO₂ thickness. PRS spectral intensity and Si surface stress obtained from PRS spectrum as a function of ZrO₂ thickness are shown in Fig. 4.29. PRS spectral intensity decreases with increasing ZrO₂ thickness. This result can be explained by Fig. 2.18. Moreover, PRS spectrum has the large spectral intensity compared with SiO₂ in spite of thick film (cf. Fig. 3.23). This large intensity is caused by high dielectric constant of ZrO₂ film. Si surface stress decreases with increasing ZrO₂ thickness. This result means that Si surface stress is reduced in the case of thick ZrO₂ film.

Figure 4.30 shows PRS spectra of Al₂O₃/Si, ZrO₂/Si and La₂O₃/Si deposited by MOD. The film thickness of these films is about 40 nm. Despite lowest dielectric constant (≈ 11 [10]), PRS spectral intensity of Al₂O₃/Si is the largest among them. Generally, Al₂O₃/Si interface almost always has a high density of negative fixed charges [11]. If the negative charge exists in the insulator film, PRS spectral intensity increases contrary to the case of positive charge existence. Thus, very large PRS spectrum is measured for Al₂O₃/Si. On the other hand, PRS spectrum for La₂O₃/Si is very small in spite of high dielectric constant (≈ 25–30 [10]). Although his origin is not known, it is assumed that there is the large positive charge in La₂O₃ film or large interface level as the recombination center of modulation carries at La₂O₃/Si interface.

4.7 Summary

The high-κ thin film/Si structures have been characterized by PRS. From excimer laser irradiation effect, it is found that PRS spectral intensity decreases with increasing the positive charge in high-κ films.

HfO₂ deposited in N₂ atmosphere has large amount of positive charges found by smaller PRS spectral intensity. PRS spectral intensity depends on deposition temperature of both HfO₂ and PrOₓ films. This result means that dielectric constant of these films increases with increasing deposition temperature because these films are densified. The Si surface stress hardly depends on deposition temperature in the case of HfO₂. On the other hand, Si surface tensile stress of PrOₓ/Si slightly increases with deposition temperature.

PRS spectral intensity of HfO₂/Si increases with RTA treatment at temperatures up to 600°C in N₂ and O₂ atmosphere. Above 700°C, the spectral intensity decreases contrarily. This decrease is caused by a decrease in the dielectric constant of the film with the interfacial layer growth observed by XPS spectra. Similar results are obtained for PrOₓ films, but decrease of PRS spectral intensity occurs at 600°C and above. It is considered that HfO₂ is more thermally-stable than
Figure 4.28: PRS spectra of ZrO$_2$/Si structures with ZrO$_2$ films of various thicknesses, 35, 40 and 55 nm.

Figure 4.29: PRS spectral intensity (open square) and Si surface stress (closed circle) obtained from PRS spectrum as a function of ZrO$_2$ thickness.

Figure 4.30: PRS spectra of Al$_2$O$_3$/Si, ZrO$_2$/Si and La$_2$O$_3$/Si. The film thickness is about 40 nm.
PrO$_x$.

The other high-$k$ materials have been also characterized. PRS spectral intensity and Si surface stress of ZrO$_2$/Si decrease with increasing ZrO$_2$ thickness. Al$_2$O$_3$/Si structure has large PRS spectral intensity because of large amount of negative charge in Al$_2$O$_3$ film. On the other hand, La$_2$O$_3$/Si has small spectral intensity in spite of similar thickness, because La$_2$O$_3$ assumably has large positive charge or large interface level.
Reference


Chapter 5

Characterization of MFIS Structure

5.1 Introduction

As described in §1.1.2, MFIS-FET type FeRAM has been expected to be a next-generation memory. As prospective materials for ferroelectric layer of MFIS structure, SrBi$_2$Ta$_2$O$_9$ (SBT) thin films have attracted much interest recently [1]. The SBT has Bismuth-layered structure and less fatigue degradation than Pb(Zr,Ti)O$_3$ (PZT) [2–4]. However, the retention property of remanent polarization of SBT film is not so good [2,5–8]. Searching of the suitable deposition and annealing parameters is fundamental to improve retention property. In this chapter, SBT/SiO$_2$/Si structures are characterized by PRS. PRS allows quick and damage-free characterization of memorized states of SBT/SiO$_2$/Si structure without electrode formation.

5.2 Sample Preparation and Characterization

After RCA cleaning and removing native oxide, n-type Si (100) wafers ($\rho \sim 0.02 \ \Omega \ cm$) were oxidized in O$_2$ atmosphere at 700°C. Then SBT films (200–500 nm) were deposited by MOD method. The precursor solution (Kojundo Y-1 type O) was coated on SiO$_2$/Si by the spin-coater. The samples were dried at 200°C and baked at 400°C in air. These processes were repeated to obtain the film of desired thickness (4–8 times). Finally, the samples were post-annealed in O$_2$ atmosphere at 500–1000°C for 10–30 min. For $C-V$ measurement, Au top electrode and AuSb bottom electrode were deposited by vacuum evaporation (Ulvac VPC-260F). The base vacuum chamber pressure is about $2 \times 10^{-6}$ Torr. The size of top electrode is about 0.15 mm φ. The detailed preparation process of MFIS structure is shown Fig. 5.1.

The structural property of the samples was characterized by X-ray diffraction (XRD; Rigaku RINT2000). The diffracted X-ray from Cu Kα radiation source was counted through 0.15 mm slit plate. The SBT film thickness was measured by ellipsometer.
Figure 5.1: Flow chart of preparation process of MFIS structure.
5.3 PRS Spectrum of FIS Structure

Figure 5.2 shows PRS spectra of SiO$_2$ and SBT/SiO$_2$/Si stacked structures. The film thickness of SiO$_2$ and SBT are about 15 nm and 400 nm, respectively. It is found that PRS spectral intensity is enhanced by deposition of SBT film. Figure 5.3 shows XRD patterns of SBT films post-annealed at 600–900°C in O$_2$ atmosphere for 10 min. The XRD peak at $2\theta = 29.0^\circ$ indicates (115) peak of bismuth-layered ferroelectric SBT [9]. SBT (115) peak is well found above 700°C. Figure 5.4 shows PRS spectral intensity and the intensity of (115) XRD peak as a function of post-annealing temperature. It is considered that PRS spectral intensity increases with the ferroelectricity of SBT film, and Si surface potential is increased by spontaneous polarization of SBT film.

Figure 5.5 shows PRS spectra of SBT/SiO$_2$/Si structures films which have various SBT thickness. The spectral shape significantly varies with SBT thickness. The SBT film is thick (> 100 nm) and has large refractive index ($\sim 2.3$ [10]) so that it may be considered that the phase of PRS spectrum changes with thickness. However, it seems that the spectral shape change of measured PRS spectrum is more drastic than that of calculated one. The SBT film is not transparent perfectly (transmittance: 20–50% [10]) at spectral range of measured PRS spectrum, so the refractive index has the imaginary part. Moreover, the transmittance depends on photon energy. Therefore, it is considered that the spectral shape change of measured PRS spectrum do not agree well than that of calculated one.
5 Characterization of MFIS Structure

Figure 5.2: PRS spectra of SiO₂/Si and SBT/SiO₂/Si structures.

Figure 5.3: XRD patterns of SBT/SiO₂/Si structures annealed at different temperatures. SBT thin films were deposited by sol-gel method.

Figure 5.4: PRS spectral intensity and XRD intensity of (115) peak as a function of post-annealing temperature.
Figure 5.5: PRS spectra of SBT/SiO$_2$/Si structures with various SBT thickness.
5.4 Memorized States of MFIS Capacitor

To characterize of memorized states of SBT/SiO$_2$/Si structures, it was poled by DC voltage without electrode. The bottom of the sample (with native oxide) was grounded during poling process. After poling of SBT film, SBT/SiO$_2$/Si structure was measured by PRS, as shown in Fig. 5.6.

5.4.1 Poling Effect

Figure 5.7 shows PRS spectra of poled SBT/SiO$_2$/Si structure. PRS spectral intensity greatly increases by $-3$ V poling. PRS spectral intensity as a function of applied poling voltage is shown in Fig. 5.8. The spectral intensity has exponential dependence on poling voltage. If negative voltage is applied, Si surface potential is enlarged by remanent polarization in SBT layer, as solid line in Fig. 5.9, so that PRS spectral intensity increases as shown by eq. (2.103).

PRS spectral intensity of PRS also depends on modulation laser power $P_m$ (eq. (2.103)). The Si surface potential $\Psi_s$ can be estimated by the experimental data with theoretical curve of eq. (2.103). Figure 5.10 shows PRS spectral intensity as a function of power of modulation light (open square) and fitted curve (dashed line) using by eq. (2.103). The theoretical curve is well fitted to experimental data. Si surface potential obtained by curve fitting is shown in Fig. 5.11. Si surface potential linearly increases with increasing negative poling voltage. The increase of Si surface potential by $-1$ V poling is $0.17$ eV.

Figure 5.12 shows PRS spectra normalized by peak intensity of negative poled SBT/SiO$_2$/Si. The shift to low energy side of PRS spectrum increases with increases negative poling voltage. Figure 5.13 shows $E_1$ critical point obtained by curve fitting of PRS spectrum and Si surface stress calculated using eq. (3.10) as a function of poling voltage. $E_1$ linearly decreases with increasing negative poling voltage. This result means increase of tensile stress at Si surface. The SBT film has not only ferroelectricity but also piezoelectricity. The relationship between electric displacement $D$ ($= P_s$: remanent polarization) and stress $T$ of SBT film without external electric

![Diagram](image-url)
Figure 5.7: PRS spectra of poled SBT/SiO$_2$/Si structure.

Figure 5.8: PRS spectral intensity as a function of poling voltage.

Figure 5.9: Band diagram of FIS structure. The arrows in ferroelectric layer express direction of remanent polarization. Solid line shows the case of negative polarization and dashed line shows the case of positive polarization.
field is expressed as a following equation [11],

\[ D = P_s = dT, \]  

(5.1)

where \( d \) is piezoelectric constant. It is considered that Si surface stress is increased by piezoelectric effect of SBT film throughout SiO2 layer. The poling at −3 V induces tensile stress of \(~30\) MPa.

Figure 5.14 shows the Raman spectra of SBT/SiO2/Si structure poled at −5 V and 0 V. The peak shift of Raman spectra is hardly observed. This result means that the small stress induced by ferroelectric layer which cannot be observed by Raman spectroscopy can be characterized by PRS spectra.

### 5.4.2 Retention Property

The retention property of memory of SBT/SiO2/Si structure was characterized by utilizing PRS. The time dependence of PRS spectrum of SBT/SiO2/Si structure after poling −5 V and hold at 0 V is shown in Fig. 5.15. PRS spectral intensity gradually decreases after poling. Figure 5.16 shows the time dependence of difference of retained capacitances of SBT/SiO2/Si written at +5 V and −5 V (open square), and the time dependence of PRS spectral intensity (close circle). It is found that these time dependencies show the same tendencies. Si surface potential decreases with decreasing charge injection or the remanent polarization in SBT film. Therefore, it is considered that PRS spectral intensity in Fig. 5.16 reflects retention property of SBT film so that retention property of MFIS structure can be characterized by contactless measurement of PRS spectral intensity.
5.4 Memorized States of MFIS Capacitor

Figure 5.12: PRS spectra normalized by peak intensity of negative poled SBT/SiO$_2$/Si.

Figure 5.13: $E_1$, transition energy at critical point obtained from PRS spectrum as a function of poling voltage.

Figure 5.14: Raman spectroscopy of SBT/SiO$_2$/Si structure poled at $-5$ V and 0 V.
5 Characterization of MFIS Structure

Figure 5.15: Time dependence of PRS spectrum of SBT/SiO$_2$/Si structure. Writing (poling) voltage is $-5$ V and holding voltage is $0$ V.

Figure 5.16: Time dependence of retained capacitance of SBT/SiO$_2$/Si (open square), and the time dependence of PRS spectral intensity (close circle).

It has been reported that the memory retention property of SBT/SiO$_2$/Si is significantly improved by RTA after deposition [7]. And the crystallographic structure of SBT [12] and (Bi, La)$_4$Ti$_3$O$_{12}$ (BLT; has Bi layered structure as well as SBT) [13] thin film is also improved by RTA for each spin-coated layer (layer-by-layer RTA). Consequently, we have confirmed the improvement of retention property of SBT/SiO$_2$/Si structure by layer-by-layer RTA using PRS. RTA process were performed after spin-coating and drying for 30 sec (see § 5.1). The post-annealing also performed in RTA furnace for 30 min. The atmosphere and temperature of RTA were O$_2$ and 750°C, respectively. Figure 5.17 shows PRS spectral intensity of SBT/SiO$_2$/Si deposited by conventional process (open square) and that deposited by layer-by-layer RTA process (close circle). The decrease of PRS spectral intensity for layer-by-layer RTA is obviously smaller than that for conventional process. It is considered that improvement of memory retention property of SBT/SiO$_2$/Si structure is observed by PRS measurement without electrode formation.

5.4.3 Characterization of Hysteresis without Electrode Formation

To apply voltage during PRS measurement, a plate glass with indium tin oxide (ITO) transparent electrode was firmly attached to the sample, as shown in Fig. 5.18. Thickness of ITO film is about 200 nm.

Figure 5.19 shows the dependence of PRS spectra on applying voltage after ±5 V poling. The spectral intensity depends on the direction (plus or minus) of poling voltage. (the intensity with applying 0 V after $-5$ V poling is larger than that after $+5$ V poling). Figure 5.20 shows applied voltage dependence of PRS spectral intensity after ±5 V poling. The spectral intensity has a clockwise hysteresis loop. The $C$-$V$ curve of Au/SBT/SiO$_2$/Si is shown in Fig. 5.21. The curve
Figure 5.17: PRS spectral intensity of SBT/SiO₂/Si deposited by conventional process (open square) and that deposited by layer-by-layer RTA process (close circle).

Figure 5.18: PRS measurement with attaching ITO transparent electrode.
5 Characterization of MFIS Structure

Figure 5.19: Dependence of PRS spectra on applying voltage after ±5 V poling.

Figure 5.20: Applied voltage dependence of PRS spectral intensity. Open squares show the case after −5 V poling and open triangles show the case after +5 V. shows a counterclockwise hysteresis loop which signifies the ferroelectricity. The hysteresis of PRS spectral intensity has reverse loop toward C-V curve.

The D-E hysteresis loop of ferroelectric is expressed by Miller’s equation [14].

\[ D_{sat}^± = \pm P_s \tanh \left[ \frac{±E − E_c}{2\delta} \right] + \varepsilon_0 \varepsilon_f E, \]  

(5.2)

where

\[ \delta = E_c \left( \ln \left( \frac{1 + P_r/P_s}{1 − P_r/P_s} \right) \right)^{-1}, \]  

(5.3)

\( P_r \) and \( P_s \) are the remanent polarization and spontaneous polarization, \( E_c \) is coercive force, and \( \varepsilon_f \) is the ferroelectric linear dielectric constant. Hence, capacitance of ferroelectric layer (thickness: \( d_f \)) is expressed as follows,

\[ C_f^± = \frac{dD}{dE} \frac{1}{d_f} = \frac{P_s}{2\delta} \text{sech}^2 \left[ \frac{±E − E_c}{2\delta} \right] + \varepsilon_0 \varepsilon_f. \]  

(5.4)

Assuming that there is no charge at interfaces and in insulator film, electric density is continuous through MFIS stack from Gauss’ low [15]. So, the space charge density at Si surface (\( Q_s \)) expressed by eq. (2.106) equals to \( D_{sat}^± \). The capacitance of MFIS structure is obtained by

\[ C = \left( \frac{1}{C_f^±} + \frac{1}{C_i} + \frac{1}{C_D} \right)^{-1}, \]  

(5.5)

where \( C_i \) and \( C_D \) are capacitances of insulator (thickness: \( d_i \)) and dipletion layer of Si surface, respectively [16],

\[ C_i = \frac{\varepsilon_i}{d_i} \]  

(5.6)
5.4 Memorized States of MFIS Capacitor

\[ C_D = \frac{\partial Q_s}{\partial \Psi_s} = \frac{\varepsilon_s}{\sqrt{2}L_D} \left( 1 - e^{\frac{\Psi_s}{kT}} + \frac{p}{n} \left( e^{\frac{\Psi_s}{kT}} - 1 \right) \right) F(\Psi_s), \]  

(5.7)

and \( F(\Psi_s) \) is expressed by eq. (2.107). C-V curve can be calculated by using eqs. (2.108) and (5.5). PRS spectral intensity can be calculated by obtaining \( \Psi_s \) from eq. (5.7) and substituting \( \Psi_s \) to eq. (2.103).

Figure 5.22 shows calculated C-V curve and PRS spectral intensity as a function of applied voltage. The values used for calculation are shown Table 5.1. The directions of hysteresis are same as measured data (Figs. 5.20 and 5.21). Therefore, it is considered that the hysteresis loop of PRS spectral intensity reflects ferroelectricity of SBT film as well as C-V curve.
Table 5.1: Conditions for calculation of MFIS structure.

<table>
<thead>
<tr>
<th>Ferroelectric layer</th>
<th>Insulator layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c$ 35 kV/cm</td>
<td>$\varepsilon_i$ 3.9</td>
</tr>
<tr>
<td>$P_r$ 10 $\mu$C/cm$^2$</td>
<td></td>
</tr>
<tr>
<td>$P_s$ 12 $\mu$C/cm$^2$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_f$ 248</td>
<td></td>
</tr>
</tbody>
</table>

5.5 Summary

SBT/SiO$_2$/Si structures have been characterized by PRS. PRS spectral intensity increases by deposition of SBT film because of spontaneous polarization in SBT film. PRS spectral intensity is closely related to SBT (115) peak intensity in XRD pattern. It is considered that PRS spectrum reflects the ferroelectricity of SBT film.

PRS spectral intensity linearly increases with negative poling voltage because of Si surface potential is enlarged by remanent polarization in SBT. The holding time dependence of PRS spectral intensity is measured. PRS spectral intensity gradually decreases as well as capacitance difference of $C$-$V$ curve. Moreover, decrease of PRS spectral intensity is reduced by introduce of RTA process. It is considered that the memory retention property of SBT/SiO$_2$/Si can be characterized by time dependence of PRS spectral intensity.

The spectral intensity reflects hysteresis characteristic of SBT/SiO$_2$/Si structure. From these results, it is considered that PRS can be applied to characterization of ferroelectricity in MFIS structures as a contactless measurement.
Reference


Chapter 6

Conclusions

The principal results obtained in this thesis work are summarized as follows:

1. PRS spectral intensity has been calculated from Si surface potential as a function of dielectric constant and thickness of insulator film. It has been shown that properties of insulator film can be characterized by PRS spectral intensity. (Chap. 2)

2. $E_1$ critical point obtained from PRS spectrum linearly decreases with increasing tensile stress at Si surface. The decrease of $E_1$ is 0.01 eV per 10 MPa. It has been shown that the Si surface stress can be estimated by PRS. (Chap. 3)

3. Si surface stress caused by thermally oxidation decreases with increasing oxidation temperature. Estimated tensile stress is 150 MPa for 600°C oxidation and 90 MPa for 800°C oxidation. (Chap. 3)

4. The relationship between PRS spectral intensity and oxygen defects in HfO$_2$ film induced by excimer laser irradiation has been investigated. It has been brought out that PRS spectral intensity is reduced by existence of positive charges caused by oxygen defects. (Chap. 4)

5. Deposition and RTA conditions of HfO$_2$ thin films have been evaluated by PRS. For deposition in N$_2$ atmosphere, PRS spectral intensity becomes small because of positive charge caused by oxygen defects. PRS spectral intensity is increased by RTA at up to 600°C in N$_2$ or O$_2$, and decreased for more than 600°C because of interfacial layer growth. (Chap. 4)

6. Deposition and RTA conditions of PrO$_x$ thin films have been evaluated by PRS. It is found that PrO$_x$ film which has small oxygen defects and high dielectric constant can be obtained by deposition in O$_2$ atmosphere at high temperature (400°C). The interfacial layer growth is obviously observed by RTA at 600°C and above found by decrease of PRS spectral intensity. (Chap. 4)
7. PRS spectral intensity significantly increases and shifts to low energy side with poling of SBT/SiO$_2$/Si structure by negative voltage. The change of spectral intensity reflects increase of Si surface potential by remanent polarization in SBT film. Si surface potential obtained by dependence of PRS on modulation light power increases 0.17 eV by $-1$ V poling. (Chap. 5)

8. The memory retention property of SBT film has been characterized by PRS spectral intensity. The spectral intensity decreases with decrease of remanent polarization as time passes. Using RTA process for deposition, decrease of PRS spectral intensity is suppressed. This means that the improvement of retention property can be characterized by contactless PRS. (Chap. 5)

9. PRS measurement with applying voltage using ITO transparent electrode has been performed. PRS spectral intensity shows a hysteresis characteristic which reflects C-V curve. (Chap. 5)
Vita

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Publications

Academic Journals


Proceedings of Conferences


Presentation of International Conferences


Domestic Meetings


Index

C-V curve, 61, 64, 92
Airy function, 10
Al$_2$O$_3$, 75
band diagram, 30, 47
BLT, 90
broadening factor, 13
Deal-Groove model, 45
Debye length, 30
dielectric function, 11, 13
ellipsometry, 50, 81
ESR, 61
fixed charge, 3, 31, 57, 61, 64, 75
Franz-Keldysh effect, 5, 12
HfO$_2$, 57, 64
high-k material, 1, 57
hysteresis loop, 90
interfacial layer, 3, 64, 71
ITO electrode, 90
La$_2$O$_3$, 75
laser ablation, see PLD
MFIS structure, 4, 86
retention property, 4
Miller’s equation, 92
MOD, 58, 81
native oxide, 45
oxide charge, see fixed charge
oxygen vacancy, 61, 64, 71
penetration depth, 33
photoreflectance spectroscopy, 4
curve fitting, 33
dependence on thickness and refractive
index of film, 26
measurement setup, 33
spectral intensity, 28, 29
film thickness dependence, 30
positive charge dependence, 31
third derivative form, 26
piezoelectric effect, 86
PLD, 58
Poisson’s equation, 28
Poisson’s ratio, 40
poling, 86
PrO$_x$, 57, 71
PZT, 81
Raman spectroscopy, 50, 88
remanent polarization, 86, 88
retention property, 81, 88
RTA, 58, 66, 71, 90
SBT, 81
Schottky barrier, 29
Schrödinger equation, 9
Seraphin coefficient
complex form, 25
normal incidence, 16
oblique incidence, 18
through 1 layer, 22
through 2 layers, 25
Si diaphragm structure, 39
Si surface potential, 30, 86
Si surface strain, 40
Si surface stress, 41, 42, 47, 50, 71, 86
SiO$_2$, 50
Snell’s low, 17, 20
space charge, 30
thermal oxidation, 50
third derivative theory, 5, 13
XPS, 45, 50
XRD, 81, 83
Young’s modulus, 40
ZrO$_2$, 75