Contactless Characterization of Fixed Charges in HfO$_2$ Thin Film by Photoreflectance

Masayuki Sohgawa$^1$, Masato Yoshida$^1$, Takuji Naoyama$^1$, Taizou Tada$^1$, Kouji Ikeda$^1$, Takeshi Kanashima$^1$, Akira Fujimoto$^2$ and Masanori Okuyama$^1$

$^1$Area of Advanced Electronics and Optical Science, Department of Systems Innovation, Graduate School of Engineering Science, Osaka University

1 Department of Electrical Engineering, Wakayama National College of Technology

Fixed oxide charges in HfO$_2$ thin films have been characterized by photoreflectance spectroscopy (PRS). HfO$_2$ films were deposited on Si by pulsed laser deposition (PLD) in N$_2$, O$_2$ and mixture of these gases. PRS spectral intensity decreases with increasing positive charge in a film. HfO$_2$ deposited in N$_2$ has larger positive charges than that deposited in O$_2$, because of smaller PRS spectral intensity of the former. It is confirmed by ArF laser irradiation that this positive charge is caused by oxygen defects in HfO$_2$. Moreover, the effects of rapid thermal annealing (RTA) on HfO$_2$/Si have been evaluated by PRS. The PRS spectral intensity becomes maximum by RTA at 600°C in N$_2$ or O$_2$. It is suggested that the suitable temperature for the RTA treatment of the HfO$_2$/Si structure prepared by PLD is 600°C.

KEYWORDS: photoreflectance spectroscopy (PRS), pulsed laser deposition (PLD), hafnium oxide (HfO$_2$), fixed charge, Si surface potential

1. Introduction

In recent years, high-$k$ oxide thin films have received considerable attention for application in gate insulator films in ultralarge-scale integrated (ULSI) circuits to suppress direct tunneling current through a gate insulator.$^1$ The thickness of SiO$_2$ films should be less than 1 nm for high-performance logic,$^2$ but such films have a very large direct tunneling current so that they cannot be used because of their large power dissipation. A high-$k$ gate insulator could suppress such leakage exponentially through the increase in film thickness without the degradation of the control of drain current. For high-$k$ gate oxide materials, ZrO$_2$$^{3,4}$ HfO$_2$$^{5,6}$ and lanthanoid oxides$^{4,7,8}$ have been investigated because of their stability to silicon substrate and their high permittivity. In particular, HfO$_2$ and their silicates$^9$ or aluminates are promised for gate oxides. However, since their films have larger interfacial states and larger fixed charges than those of SiO$_2$, the characteristics of devices, such as threshold voltage and carrier mobility, are affected.

Photoreflectance spectroscopy (PRS), a type of modulation reflectance spectroscopy, is a
nondestructive and contactless characterization method that can be applied to in-situ characterization. Moreover, it is very sensitive to energy band structures at surfaces and interfaces because the penetration depth of the probe light is about 10 nm in the spectral range at the E\textsubscript{1} critical point ($\sim 3.4$ eV) in Si\textsuperscript{10} and is easily measurable in air at room temperature. PRS spectral intensity sensitively reflects Si surface potential (band bending) which varies with charges in the film. We have characterized plasma-induced damage\textsuperscript{11} and stress\textsuperscript{12} at Si surfaces, the charging damage of a gate oxide\textsuperscript{13} and PrO\textsubscript{x}/Si structures\textsuperscript{14} by PRS. In this study, we characterize fixed charges in HfO\textsubscript{2} films by PRS without an electrode.

2. Theory

When the Si surface is irradiated with modulation light, photocarrier generation occurs, which induces a change in the surface potential of Si. Dielectric function is modulated by this perturbation of the surface field, and this change is sharply reflected in the optical property around the band edge. The PRS spectrum, which is the ratio of reflectance variation by laser irradiation to reflectance ($\Delta R/R$) is expressed by eq. (1) as a function of photon energy ($E$).\textsuperscript{15}

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

Here, $A$ and $\theta$ are the intensity and phase factors of the spectrum, respectively, $E_{CP}$ is the critical point energy of the Si energy band structure, $\Gamma$ is the broadening factor of the spectrum, and $n$ is the number dependent on the dimensionality of the band edge, such as 3 for the E\textsubscript{1} ($\Lambda_3$-$\Lambda_1$) critical point. PRS spectral intensity ($|A|$) is expressed as a function of Si surface potential ($\Psi_s$).\textsuperscript{16}

$$|A| \propto \ln \left[ B \exp \left( \frac{\Psi_s}{kT} \right) + 1 \right]$$

Here $B$ is a constant.

Figure 1 shows energy band diagrams of the insulator/Si (n-type) structure. In the structure shown in Fig. 1 (a), the voltage at the insulator surface ($V$) is expressed as a function of Si surface potential ($\Psi_s$).\textsuperscript{17}

$$V = \frac{\Psi_s}{q} + \frac{d}{\varepsilon_i} \sqrt{\frac{2\varepsilon_s kT}{q L_D}} F(\Psi_s)$$

Here $F(\Psi_s)$ is shown by

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

$$L_D = \sqrt{\frac{\varepsilon_s kT}{q^2 n}}$$

where, $\varepsilon_i$ and $\varepsilon_s$ are the dielectric constants of the insulator and Si, and $n$ and $p$ are the equilibrium densities of electrons and holes, respectively. $\Psi_s$ can be obtained by numerically solving eq. (3). Then the PRS spectral intensity can be calculated using eq. (2). Figure 2
Fig. 1. Band diagrams of insulator/Si structure for (a) ideal case, and (b) case of existence of positive charge in insulator.

Fig. 2. Dependence of PRS spectral intensity (|A|) on insulator thickness (d) calculated from eqs. (2) and (3).

shows the dependence of PRS spectral intensity (|A|) on the insulator thickness (d) calculated from eq. (2) by substituting $\Psi_s$ obtained by numerical calculation using eq. (3), 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 ($Q_o$) (per unit area) in the insulator
The dependence of PRS spectral intensity $|A|$ on the positive oxide charge $Q_o$ calculated using eqs. (2) and (4) is shown in Fig. 3. It is found that spectral intensity decreases with increasing positive charge.

3. Experimental

n-Type Si (100) substrates were used for PRS and ESR, and p-type Si (100) were used for electric characterization. After RCA cleaning, the native oxide was removed with dilute HF. HfO$_2$ films were deposited on substrates by pulsed laser deposition (PLD). The substrate temperature was 400°C and the deposition atmospheres used were O$_2$, N$_2$ and a mixture of these gases. Some samples were treated by rapid thermal annealing (RTA) in N$_2$, O$_2$, H$_2$(5%)/N$_2$ (known as a forming gas) atmosphere at 300–800°C. For the C-V measurement, an Al electrode was deposited by vacuum evaporation. Details of the deposition and annealing conditions are shown in Table. I.

The samples were characterized by PRS, transmission electron microscopy (TEM), ESR, X-ray photoelectron spectroscopy (XPS) and C-V measurement. For PRS, the surface potential of the sample was modulated with an Ar$^+$ laser (wavelength: 488 nm) intermitted by a mechanical chopper. Simultaneously, the sample was irradiated with a probe light from a Xe discharge lamp and reflected light from the sample was guided to the monochromator. The light dispersed by the monochromator was detected by a photomultiplier. A small change in
Table I. Deposition and RTA conditions.

<table>
<thead>
<tr>
<th>Deposition conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sintered target</strong></td>
<td>HfO$_2$ ceramic</td>
</tr>
<tr>
<td><strong>Substrate</strong></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 C-V measurement</td>
</tr>
<tr>
<td><strong>Substrate temperature</strong></td>
<td>100–400°C</td>
</tr>
<tr>
<td><strong>Gas</strong></td>
<td>O$_2$, N$_2$</td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>0.2 Torr</td>
</tr>
<tr>
<td><strong>Laser</strong></td>
<td>ArF excimer laser</td>
</tr>
<tr>
<td><strong>Repetition frequency</strong></td>
<td>1.0 Hz</td>
</tr>
<tr>
<td><strong>Shot energy</strong></td>
<td>130 mJ/shot</td>
</tr>
<tr>
<td><strong>Target-substrate distance</strong></td>
<td>40–60 mm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Annealing (RTA) conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atmosphere</strong></td>
<td>N$_2$, O$_2$, H$_2$(5%)/N$_2$ (forming gas)</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>400–800°C</td>
</tr>
<tr>
<td><strong>Hold time</strong></td>
<td>0 s</td>
</tr>
</tbody>
</table>

Fig. 4. PRS spectra of HfO$_2$/Si deposited in O$_2$, N$_2$ and a mixture gas.

reflectance ($\Delta R$) was detected by a lock-in amplifier referring to chopping frequency. All PRS measurements were performed in air at room temperature.
4. Results and Discussion

Figure 4 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). PRS spectral intensity depends on the deposition atmosphere. The positive oxide 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. 5. 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 defects. On the other hand, the 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 shown in Fig. 3. Thus, a large positive charge can be obtained by decreasing PRS spectral intensity.

The PRS intensity of HfO$_2$/Si deposited in O$_2$ is smaller than that of HfO$_2$/Si deposited in
Fig. 7. PRS spectral intensity as a function of number of laser shots normalized by PRS spectral intensity of as-deposited sample.

Fig. 8. ESR spectra of HfO$_2$/Si structure without and with ArF laser irradiation.

the gas mixture in spite of the smaller charge density of the former. Assuming that the voltage at the film surface ($V$) is constant, PRS intensity decreases with decreasing dielectric constant or increasing film thickness for the HfO$_2$ film, as shown in Fig. 2. Figure 6 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. 6 (a)). Similar results are obtained by measurement of the XPS spectrum of Si 2p. From these results, it is considered that a small PRS spectral intensity is caused by lower dielectric constant because of the interfacial layer growth.
To identify the origin of the positive charge in HfO$_2$ film, the samples were irradiated with ArF excimer laser light in air at room temperature. Figure 7 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. Figure 8 shows the ESR spectra of HfO$_2$/Si structure with and without ArF laser irradiation. The peak at approximately $g \approx 2.003$ increases with the laser irradiation. It is considered that this peak arises from oxygen defects in the HfO$_2$ film, not from interface defects, since it is independent of the direction of the magnetic field.$^6$ The C-V curves of the Al/HfO$_2$/Si structure with and without the laser irradiation are shown in Fig. 9. The C-V curves shift to the negative voltage direction and accumulation capacitance is decreased by the laser irradiation. This result implies that the positive charge in the HfO$_2$ film increases with the laser irradiation. From the ESR results (Fig. 8), the laser irradiation generated unpaired electrons induced by oxygen defects in the HfO$_2$ film. It is considered that the dangling bonds of Hf atoms are generated by the laser irradiation. Therefore, the HfO$_2$ film becomes positively charged as a result of these dangling bonds. If the positive charge in the film increases, Si surface potential decreases and consequently PRS spectral intensity decreases, as shown in Fig. 3. In addition, the accumulation capacitance shown in Fig. 9 shows a tendency to decrease with increasing number of laser shots. Although the cause of this is not with experimentally confirmed, it is assumed that the dielectric constant of the film decreases with oxygen defect formation in the film generated by the laser irradiation, because it is unlikely that the film thickness increases by the laser irradiation. Nevertheless, PRS spectral intensity also decreases with decreasing dielectric constant of the HfO$_2$ film.

PRS was utilized for the characterization of RTA in N$_2$, O$_2$ and a forming gas. The
dependence of PRS spectral intensity on RTA temperature in these atmospheres are shown in Fig. 10. The PRS spectral intensity of what annealed at 600°C are larger than that of what annealed at 500°C for RTA in N₂ and O₂. On the other hand, the increase in PRS intensity occurs up to 500°C for RTA in the forming gas. As discussed previously, PRS intensity decreases with increasing positive charge in the film. Therefore, it is considered that the reduction in the number of positively charged defects in HfO₂ by RTA is found by PRS. The spectral intensity rapidly decreases at 700°C and above for RTA in N₂ and O₂. On the other hand, for RTA in the forming gas, it decreases at 600°C, which is a lower temperature than those for the other atmospheres. Figure 11 shows the XPS spectra of the Si 2p of HfO₂/Si structure treated by RTA. The chemical-shifted peak of Si 2p rapidly increases at high temperatures. This result means that an interfacial layer (including Hf-silicate and SiO₂) grows by RTA at high temperatures. Similar results are obtained by TEM. The interfacial growth for O₂ RTA is larger than that for N₂ RTA, and the increase in the area of an interfacial layer for forming gas RTA occurs at a lower temperature than those for the other atmospheres. 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 HfO₂, as shown in Fig. 2. It is suggested by these PRS results that suitable temperatures for the RTA of HfO₂/Si structure are 600°C in N₂ or O₂, and 500°C in the forming gas.

5. Conclusions

HfO₂ film on Si has been characterized by PRS. Comparing the C-V curves, it is found that the PRS spectral intensity of HfO₂/Si deposited in N₂ is smaller than those of HfO₂/Si deposited in N₂ and the mixture gas because of the large amount of positive charge formed in the HfO₂ film. PRS spectral intensity decreases with ArF excimer laser irradiation. The decrease in the spectral intensity is caused by the generation of positively charged defects in HfO₂ film which is estimated by ESR and C-V measurements. PRS spectral intensity increases with RTA treatment at temperatures up to 600°C in N₂ and O₂ atmosphere. At 700°C and above, 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. Thus, it has been demonstrated that PRS is very sensitive for fixed charges in HfO₂ and interfacial layer growth, and can be applied to in-situ characterization.

Acknowledgment

Part of the present experiments was carried out in a facility in the Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University.
Fig. 10. Dependence of PRS spectral intensity on RTA temperature in (a) N₂, (b) O₂ and (c) forming gas.
Fig. 11. XPS spectra of Si 2p of HfO$_2$/Si treated by RTA in (a) N$_2$, (b) O$_2$ and (c) forming gas.
References


2) International Technology Roadmap for Semiconductors (SEMA TECH, Austin, TX, 2003) p. 11.


