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Contactless Characterization of Fixed Charge in HfO_2 Thin Film by Photoreflectance

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1. Introduction

Recently, high-k oxide thin films have captured the attention for application to gate insulator films of ultra-large-scale integrated circuit (ULSI) to suppress the direct tunneling current through gate insulator and enhance the reliability of ULSI devices[1]. For high-k gate oxide material, HfO_2, their silicates or aluminates have been investigated extensively because of their stability to silicon substrate and high permittivity. However, since their films have more interface states and fixed charges than SiO_2, it affects characteristics of devices such as threshold voltage and carrier mobility.

Photoreflectance spectroscopy (PRS), a type of modulation reflectance spectroscopy, is non-destructive and contactless characterization method so that can be applied to *in-situ* characterization. Moreover, it is very sensitive to energy band structure at surface and interface because the penetration depth of the probe light is about 10 nm in the cases of spectral range for E_1 critical point (~ 3.4 eV) in Si. PRS spectral intensity sensitively reflects the Si surface potential (band bending) which varies with the charge in the film. In this work, we have characterized the fixed charge in HfO_2 film by PRS without electrode.

2. Experimental

The n-type Si (100) substrates were used for PRS and p-type Si (100) for the electric characterization. After RCA cleaning, native oxide was removed by HF treatment. HfO_2 films were deposited on substrates by pulsed laser deposition (PLD) method. The substrate temperature was 400°C and the atmosphere were O_2, N_2 and mixture of these gases. Some samples were treated by rapid thermal annealing (RTA) in N_2 atmosphere at 500-800°C.

The samples were characterized by PRS, electron spin resonance (ESR), X-ray photoelectron spectroscopy (XPS) and *C-V* measurement. For PRS measurement, the surface potential of the sample was modulated by Ar^+ laser intermitted by a mechanical chopper. Simultaneously the sample was irradiated by a probe light from Xe discharge lamp and reflected light from sample was guided to the monochromator. The dispersed light by the monochromator was detected by the photo-multiplier. A small change of reflectance (ΔR) was measured by a lock-in amplifier referring to the chopping frequency.

3. Results and Discussion

Figure 1 shows PRS spectra of samples deposited in O_2, N_2 and mixture gas (O_2:N_2=2:1). The PRS spectral intensity depends on deposition atmosphere. The charge density in HfO_2 film calculated from flat band voltage shift of *C-V* curve and PRS spectral intensity are shown in Fig. 2. The spectral intensity of PRS is expressed as a following function of Si surface potential Ψ_s[2],

$$\left|\frac{\Delta R}{R}\right| \propto \ln\left\{A\exp\left(\frac{\Psi_s}{kT}\right)+1\right\}, \qquad (1)$$

where A is a constant. If there is positive charge in the film, Ψ_s is decreased in the case of n-type Si. PRS spectral intensity decreases with decreasing Ψ_s from eq. (1). It is considered that there are more positive charges in the film deposited in N_2, which is assumably caused by oxygen defect, as shown in the insets of Fig. 1.

On the other hand, PRS intensity of the sample deposited in O_2 is smaller than that in the mixture gas in spite of smaller charge density. Assuming that the voltage at film surface (V) is constant, Si surface potential decreases with

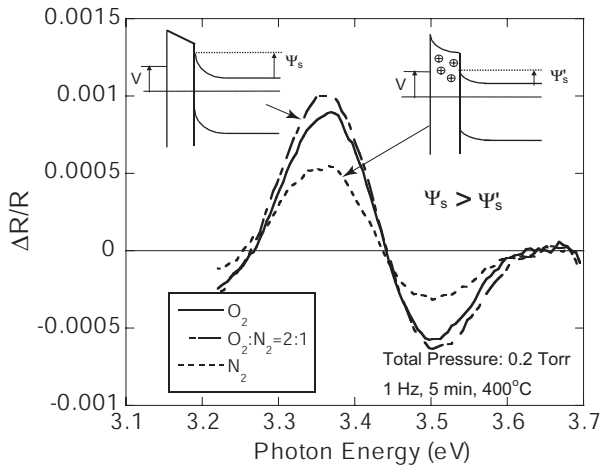

Fig. 1. PRS spectra of HfO_2/Si deposited in O_2, N_2 and these mixture gas.

decrease of dielectric constant of the film or increase of the film thickness, because the voltage applied to the film increases. The interfacial layer growth is observed by TEM image and XPS Si-2p peak in the sample deposited in O_2. Therefore, it is considered that smaller PRS spectral intensity is caused by lower dielectric constant because of the interfacial layer.

To identify the effect of the defect amount, the sample was irradiated with ArF excimer laser light. Figure 3 shows the PRS spectral intensity as a function of number of laser shot, normalized by the intensity of as-deposited sample. Spectral intensity decreases with increasing of number of laser shot. Figure 4 shows ESR spectra of the samples without and with ArF laser irradiation. The peak around g=2.003 is increased by laser irradiation. This result shows that the laser irradiation increase the defect in HfO_2 film so that PRS spectral intensity reflects the amount of oxygen defect, as shown in the insets of Fig. 3.

The PRS method was utilized for the characterization of RTA. Dependences of PRS spectral intensity and the charge density in the film on RTA temperature are shown in Fig. 5. PRS spectral intensity and charge density of the sample annealed at 600°C are larger and lower than one at 500°C, respectively. On the other hand, the spectral intensity rapidly decreases for RTA at 700°C and above. It is considered that the spectral intensity is decreased by interfacial layer growth found by XPS results. This result suggests that RTA treatment at 600°C or below is suitable for improvement of HfO_2/Si structure.

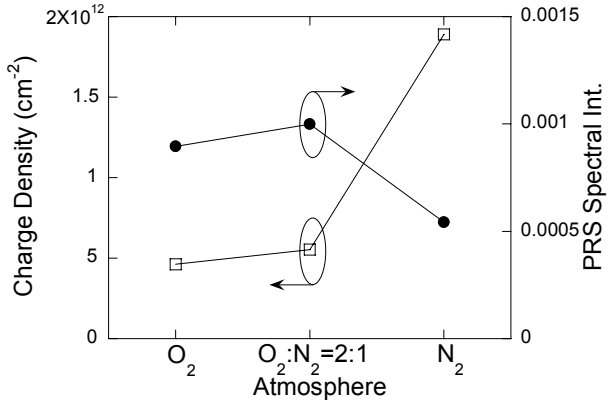

Fig. 2. The charge density in HfO_2 film calculated from flat band voltage shift of *C-V* curve and PRS spectral intensity as a parameter of deposition atmosphere.

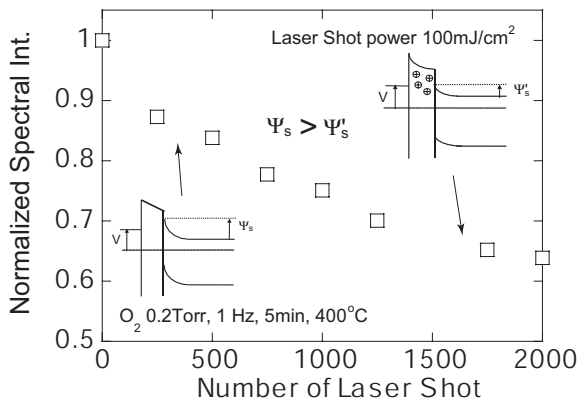

Fig.3. PRS spectral intensity as a function of number of laser shot normalized by the intensity of as-deposited sample.

4. Conclusions

HfO_2 film on Si has been characterized by PRS. Comparing with *C-V* curve, it is found that PRS spectral intensity of the sample deposited N_2 is smaller than other atmosphere because of large amount of positive charge density in the film caused by oxygen defect. PRS spectral intensity is increased by 600°C RTA treatment in N_2. At 700°C and above temperature, the spectral intensity is decreased contrarily. It is considered that dielectric constant of the film is reduced by the interfacial layer growth. As a result of this work, it has been demonstrated that PRS is very sensitive for fixed charge in HfO_2 and interfacial layer growth and can be applied to *in-situ* characterization.

References

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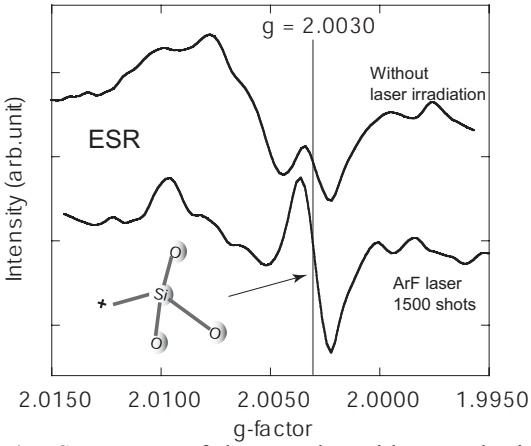

Fig. 4. ESR spectra of the samples without and with ArF laser irradiation.

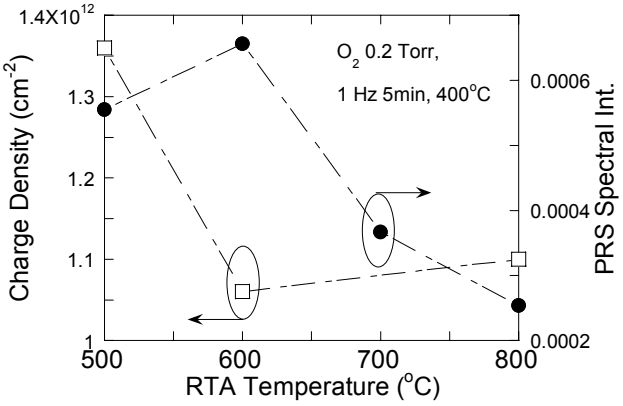

Fig. 5. Dependences of PRS spectral intensity and the charge density in the film on N_2 RTA temperature.