Extended Abstracts of the 2002 International Conference on Solid State Devices and Materials, Nagoya, 2002, pp. 54-55

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Characterization of Si Surface Stress in Various Dielectric Thin Film/Si Structure by Photoreflectance Spectroscopy

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1. Introduction

Recently, monitoring of Si surface property becomes important during the material processes for the fine fabrications of ultralarge-scale integrated circuit (ULSI). The stress at the Si surface has become an important issue because it degenerates electrical property. On the other hand, introduction of new materials, such as a high-k film and a ferroelectric film, is discussed instead of a SiO_2 film. The effects of Si surface stress under these films are must to be clarified to obtain good structure.

Photoreflectance spectroscopy (PRS) is non-destructive and contactless technique for evaluation of Si energy band structure. Moreover, it is very sensitive for the Si surface property because the penetration depth of the probe light is about 10 nm in Si. So, the PRS is recognized to be useful for monitoring technique of the Si surface stress under SiO_2 thin film by our research[1]. In this work, we have applied the PRS to measure the Si surface stress under native oxide, high-k film and ferroelectric film/SiO_2/Si structures.

2. Analysis of PRS Spectrum

When the modulation light irradiates the Si surface, photo-carrier generation occurs, and gives surface potential of Si inappreciable change. Dielectric function is changed by this perturbation of the surface field[2] and this change sharply appears around band edge. Resultantly, optical reflectance change is induced and can be measured by lock-in technique. Therefore, band structure is known by measurement of reflectance change.

According to the third derivative theory by Aspnes[3], the modulation reflectance spectrum expressed by the following in a low electric field region,

$$\frac{\Delta R}{R} = \Re\left[Ce^{i\theta}\left(E - E_g + i\Gamma\right)^{-n}\right], \qquad (1)$$

where C and θ are amplitude and phase factors, respectively, and the transition energy (E_g) and broadening factor (Γ) determine the energy location and width of the spectrum. The n value is the number dependent on dimensionality of band edge.

The stress at Si surface causes the transition energy shift at the L point[1]. If Si surface receives a tensile stress, the transition energy shifts to low energy side. We obtained following experimental equation for the stress at horizontal direction, σ_x, by straining Si diaphragm structure[1],

$$\sigma_x \approx 3540 - 1000E_g{}^L \text{ [MPa]}, \qquad (2)$$

where $E_g{}^L$ [eV] is the transition energy at the L point obtained by PRS spectrum curve fitting using eq. (1).

3. Experimental Setup and Samples Preparation

The surface potential of the sample was modulated by Ar^+ laser intermitted by a mechanical chopper. The sample was irradiated by a probe light from Xe discharge lamp. The dispersed light by the monochromator was measured by the photo-multiplier. A small change of reflectance (ΔR) was detected by a lock-in amplifier referring to the chopping frequency.

The samples are about 0.02 Ωcm n-Si (100) wafers. After chemical cleaning, silicon dioxide on Si surface was removed by HF treatment. Native oxide grown on Si was left in air after HF treatment for several months. The high-k films (PrO_x) were deposited by pulsed laser deposition (PLD)[4]. And metal/ferroelectric/thermal grown-SiO_2/Si (MFIS) structure was made. The ferroelectric ($SrBi_2Ta_2O_9$; SBT) was also deposited by PLD. Metal (Au semi transparency film) was evaporated to imply poling process.

4. Results and Discussions

(a) Monitoring of native oxide growth

Firstly the stress has been characterized in Si which is exposed to air at room temperature. Figure 1 shows the PRS spectra as a function of air exposure time. Peak intensity increases with the exposure time and peak energy position shifts to low energy (left) side. The native oxide thickness estimated by XPS is shown Fig. 2. It is found that PRS spectrum changes corresponding to oxide growth. Figure 3 shows the change of the transition energy at L point and Si surface stress obtained by eq. (2). The stress increases with native oxide growth. It is considered that oxygen atoms get into Si substrate so that expand Si lattice and tensile stress increases at its surface.

(b) PrO_x/Si interface

PRS spectra of PrO_x/Si deposited at difference substrate temperature are shown in Fig. 4. Growth temperature is the higher, PRS peak energy shift to the lower energy side. The Si surface stresses obtained by PRS are 60 MPa for room temperature, 130 MPa for 400 °C and 150 MPa for 600 °C, respectively. The higher stress is due to the fact that SiO_2 including Pr is grown at the interface between PrO_x and Si, and induces the larger stress in Si surface.

(c) SBT/SiO₂/Si structure

Figure 5 shows transition energy and Si surface stress changes after poling process. Poled SBT is strained to the direction of electric field by piezoelectric effect. On the other hand, it is compressed in the direction perpendicular to electric field. So, Si surface stress is diminished by receiving compressive stress. The broken line shows calculated one where mechanical and piezoelectric constants are linear to Si surface stress change (0 at 150 MPa). D; electric displacement is obtained from the relationship with stress, $D = d_{31}\sigma$. Since d_{31} of SBT is about 3 pC/N, D value at 50 MPa stress change is estimated to be 0.015 $\mu C/cm^2$.

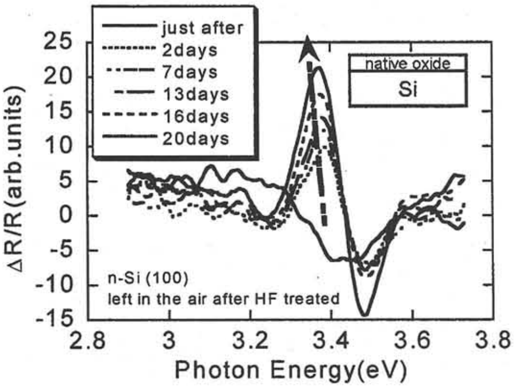

Fig. 1. PRS spectra as a parameter of exposure time in air.

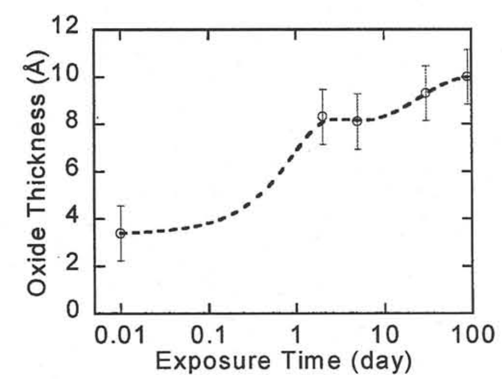

Fig. 2. Native oxide thickness on Si estimated by XPS, as a function of exposure time.

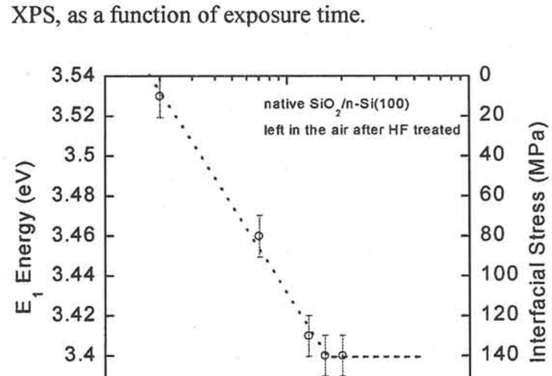

Fig. 3. Transition energy and Si surface stress in native oxide/Si as a function of exposure time.

5. Conclusions

PR spectroscopy has been applied for measurement of Si surface stress under native oxide, high-k film and MFIS structure. The Si surface stress increases with native oxide growth. The Si surface stress under PrO_x thin film deposited by PLD increases with interfacial layer growth, similarly. The stress of the surface Si is almost equal to that of PrO_x which is very important to keep amorphous state. And PRS spectrum detects Si surface stress change by piezoelectric effect of SBT over SiO_2/Si. It is considered that this result shows characteristics of ferroelectric can be obtained from PRS.

Reference

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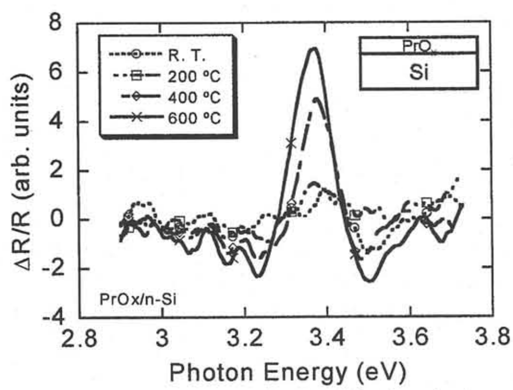

Fig. 4. PRS spectra of PrO_x/Si deposited at different growth temperatures.

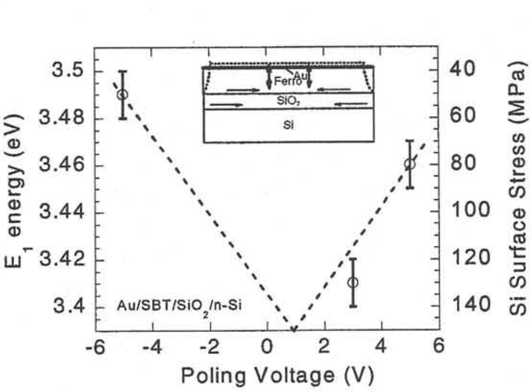

Fig. 5. Si surface stress in poled MFIS structure as a function of poling voltage..