Characterization of Surface Potential of Si-SiO₂ Interface by Photoreflectance Spectroscopy

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We have attempted to characterize $Si-SiO_2$ interface by photorefrectance(PR) spectroscopy. Si PR signal intensity was reduced by forming SiO_2 layer on the surface, but was enhanced by applying dc electric field to the $Si-SiO_2$ interface. Surface potential of Si estimated from modulation light intensity dependence of PR signal intensity decreased with increasing SiO_2 layer thickness on Si surface. The experimental results suggest that reduction of PR signal intensity of Si with SiO_2 layer was partially caused by decrease of Si surface potential.

1. Introduction

Photorefrectance(PR) spectroscopy is a contactless and nondestructive method to estimate band structure of semiconductors accurately, through the measurement of field-induced-change of the reflectance of a semiconductor whose surface potential is modulated by optically generated carriers.1) The PR method can be applied to the sample placed into plasma reaction chamber because of this method was not affected by sample ambient. We have measured surface temperature and surface potential of Si nondestructively by using this method succesfully.2) However, PR signal intensity was weakened by forming SiO₂ layer on Si surface and no PR spectra was able to be obtained if SiO₂ layer thickness was over 100Å. Therefore it was difficult to measure surface temperature and surface potential of Si-SiO₂ structure. The reduction of PR signal intensity prevented to apply this method to characterization of Si surface and interface.

In this paper, we characterize Si-SiO_2 interface by PR method and show that the PR signal intensity enhanced by applying electric field to the interface and the surface potential of Si decreased with increasing SiO_2 layer thickness on Si wafer.

2. PR spectrum measurement

Figure 1 shows energy band diagram in the vicinity of the Si-SiO₂ interface with and without light irradiation. Surface potential of Si ϕ_s (= eV_s) decreases with light irradiation for modulation as photo-generated holes accumulate at the interface. The signal in PR spectroscopy is expressed as the ratio of reflectance change induced by photo-irradiation to the reflectance.

Figure 2 shows experimental setup of PR measurement. n-type Si wafer with resistivity of 0.01 Ω cm was used as a sample. SiO₂ layer was formed on Si surface by thermal oxidation in an O₂ ambient. The sample was excited by Ar⁺ ion laser to modulate surface electric field and irradiated simultaneously by Xe discharge lamp as a probe light for measuring of surface reflectance. The



Fig.1 Energy band profile of semiconductor interface with and without light irradiation.



Fig.2 Experimental setup of PR spectroscopy.

sample was measured in the atmosphere. PR spectrum was obtained by the ratio of reflectance change to the reflectance for probe light.

Surface potential of Si $\phi_s(=eV_s)$ can be estimated by fitting the experimental modulation light intensity dependence of the PR signal intensity to the theoretical data, reported previously.²⁾ Transition energy of Si can be also calculated from PR spectra by the 3-point method based on 3rd derivative theory.

3. Result and Discussion

3.1 PR spectra under dc electric field

Figure 3 shows an example of PR spectra of Si wafer with various thickness of SiO₂ layer. Typical PR spectra are confirmed clearly around energy of 3.4 eV. Transition energy calculated from these spectra agrees with L-point transition energy of Si. Though SiO₂ layer absorbs modulation light and probe light very little, the PR signal intensities of Si decrease with increasing SiO₂ layer thickness. The PR spectrum was not observed from Si-SiO₂ structure with SiO₂ thickness over 100Å.

Figure 4 illustrate the sample structure for PR spectrum measurement of Si-SiO₂ structure with dc bias voltage. A semitransparent electrode of Au layer was deposited on the SiO, layer and electrode of Au-Sb layer was also deposited on another side by vacuum evaporation. dc bias voltage was applied by these electrodes. Excitation through and probe lights were introduced the semitransparent electrode to measure the PR spectrum. Figure 5 shows PR spectra from Si-SiO₂ structure with dc bias voltage. The thickness of SiO₂ layer was 60Å. The PR signal intensity drastically increased when dc bias voltage was applied to negative direction. The negative bias voltage increases surface potential of Si with SiO₂ layer. Taking into account the photo-generated current at the Schottky barrier, the PR spectrum intensity increased with surface potential of a sample.3) It is supposed that the



Fig.3 PR spectra of Si with various thicknesses of SiO₂ layer.

enhancement of PR signal intensity is caused by the increment of surface potential of Si.

Figure 6 shows the bias voltage dependence of the peak to peak value of PR spectrum in Si-SiO₂ structure (SiO₂:60 Å). The signal intensity increased sharply with increasing bias voltage toward negative direction and saturated at bias voltage of around -1 V. This phenomena suggests that the dc bias voltages increase the Si surface potential which is decreased by forming of SiO₂ layer on it. When the dc voltage reached -1 V, the PR signal intensity was enhanced by the factor of three to the non-biased signal. At the applied voltage beyond -1 V, the saturated intensity was determined by modulation light intensity according to the theory.³⁾



Fig.4 Configuration of Si-SiO₂ structure for increasing electric field at the interface.



Fig.5 PR spectra of Si-SiO₂ structure with various dc bias voltages. Thickness of SiO₂ layer is 60Å.



Fig.6 PR signal intensity as a function of applied bias voltage.

3.2 Surface potential of Si with SiO₂ layer

The surface potentials of $Si-SiO_2$ structure were estimated by modulation light intensity dependence of the PR signal intensity. Figure 7 shows the modulation light intensity dependence of the PR signal intensity with various thicknesses of SiO_2 layer. Solid line and broken lines show theoretical curves fitted by least mean squares method to the data. We can obtain the surface potentials of Si with SiO₂ layer from the fitted curves.

Figure 8 shows estimated surface potential of Si with various thicknesses of SiO₂ layer. The estimated surface potential of Si decreases gradually from 0.43 eV to 0.38 eV with increasing the thickness of SiO₂ layer from 24 Å to 63 Å. The tendency of the results agrees with the above discussion. We suppose that the reduction of surface potential of Si wafer by forming SiO₂ layer was caused by trap charge on the Si-SiO₂ interface, fixed oxide charge in the SiO₂ layer, or increase of the voltage applied to SiO₂ layer.

From these results, the decreasing surface potential of Si may cause to decrease PR signal intensity of Si with SiO_2 layer.

4. Conclusions

We have characterized Si-SiO₂ interface by photorefrectance(PR) spectroscopy. Si PR signal intensity was weakened by forming SiO₂ layer on the surface, but was enhanced by applying dc electric field to the Si-SiO₂ interface. Si surface potential of Si-SiO₂ structure estimated from modulation light intensity dependence of PR signal intensity decreased with increasing SiO₂ layer thickness. These results are consistent each other and suggest that diminution of surface potential of Si caused to decrease PR signal intensity of Si with SiO₂ layer partially.

By analyzing PR spectra of $Si-SiO_2$ structure, the quality of Si-SiO2 interface and/or SiO2 layer will be characterized with no contact and no destruction. This method can be used to analyze early stage of Si oxidation



Fig.7 Modulation light intensity dependence of PR signal intensity. Solid line and broken lines show theoretical curves.



Fig.8 SiO₂ thickness dependence of Si surface potential.

process and also applied *in-situ* monitoring of semiconductor manufacturing process such as growth and oxidation process even in a plasma reaction chamber.

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