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Optical Absorption in Silicon Oxide Film Near the SiO_2/Si Interface

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The contribution of SiO_2/Si interface to optical absorption below the optical absorption edge of fused quartz was studied from the measurement of change in reflectance spectra of silicon oxide films produced by chemical etching. From the modified Kramers-Kronig analysis of these reflectance considering multiple reflection in the films, it is found that optical absorption detected at the photon energy of 7.8 eV arises from Si-Si bond in the oxide film within 6 nm from the SiO_2/Si interface. The amount of Si-Si bond is evaluated to be 3×10^{14} cm^{-2}.

1. Introduction

Reflectance spectra of thermally grown silicon oxide films with thickness in the range from 6 to 17 nm were measured in the vacuum ultraviolet, and the modified Kramers-Kronig analysis considering multiple reflection in the films were applied to these spectra. Consequently, the optical properties of as grown silicon oxide films with thickness in the range from 6 to 18 nm were determined[1]. Following results were obtained from these analyses: Firstly, optical absorption below the optical absorption edge of fused quartz becomes appreciable with decreasing oxide film thickness. Secondly, optical absorption arising from Si-Si bond in the oxide film was detected. The amount of Si-Si bond in the oxide film was evaluated to be in the order of 0.3 monolayer. However, in the evaluation of amount of Si-Si bond the optical absorption tail was not considered adequately.

It is the purpose of the present study to find out the contribution of SiO_2/Si interface structures to optical absorption from the measurement of the change in reflectance spectra produced by chemical etching below the optical absorption edge of fused quartz.

2. Experimental

The specimens used for the measurement were silicon oxide films thermally grown on a p-type silicon (100) surface in dry oxygen at 800 °C and 1050 °C having thicknesses of 17.7 nm and 17.2 nm, respectively. These two oxide films were chemically etched in a dilute HF solution ($HF:CH_3OH:H_2O$ = 1:18:1) to obtain the oxide films with thickness in the range from 6 to 18 nm. Here, the etching solution with supersonic vibration was maintained at 25 °C. The oxide films with almost same thicknesses were prepared for two oxidation temperature in order to find out the effect of oxidation temperature on reflectance.

The measurements were carried out at the Beam Line 1 (BL-1) of 0.38 GeV SOR ring of Institute for Solid State Physics by using a

1 m Seya-Namioka type monochromator in the photon energy range from 4 to 23 eV. The monochromatic light, which was incident on the silicon oxide film with an incident angle of 10 degrees, was polarized in the plane of the incidence. The absolute values of reflectance were determined so that the refractive index of thermally grown silicon oxide film in the photon energy range from 5.1 to 5.4 eV was equal to that of fused quartz.

3. Results and Discussion

The solid lines in Fig. 1 shows the change in the reflectance spectra produced by chemical etching. The dashed lines in this figure indicate calculated curves for each oxide film thickness by using the optical constants of single crystalline silicon and fused quartz[2,3]. According to this figure, the decrease in reflectance in the photon energy range from 6 to 9 eV and abrupt decrease in reflectance at photon energy of 7.8 eV are observed. The effect of oxidation temperature on this abrupt decrease in reflectance is negligibly small as can be seen in Fig 2.

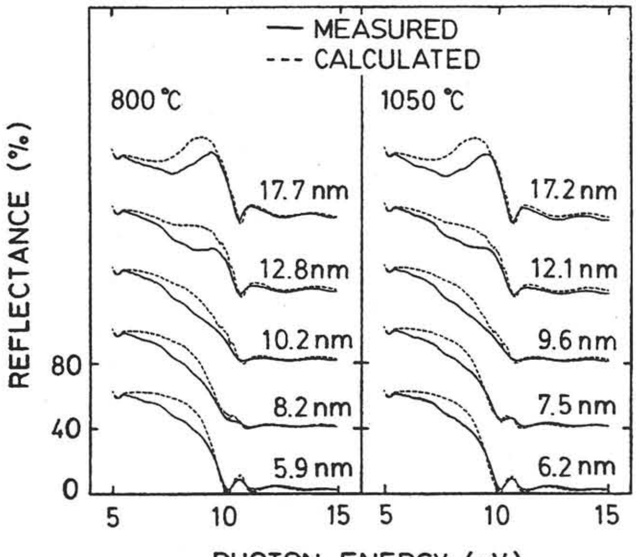

Fig. 1 The change in measured reflectance spectra caused by chemical etching are shown by the solid lines with oxide film thickness as a parameter, while calculated reflectance spectra using the optical constants of single crystalline silicon and fused quartz are shown by dashed lines. The oxide films used were grown in dry oxygen at 800 and 1050 °C.

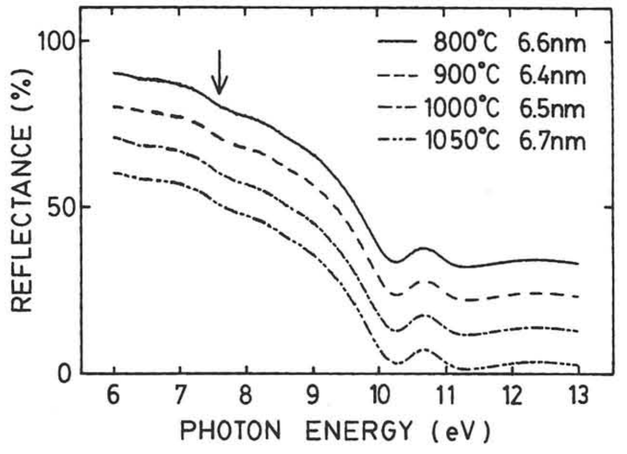

Fig. 2 Reflectance spectra of as grown oxide films grown at various oxidation temperature with almost same thickness. The reflectance spectra for oxidation temperature of 800, 900, 1000 °C are shifted upward by 30, 20, 10 % in reflectance, respectively. The arrow shows the abrupt decrease discussed in the text.

In order to find out the change in optical properties in depth direction, the optical constants should be determined. The procedure to calculate the optical constants are the same as that reported previously[1]. Namely, the phase changes on reflection, which are calculated using modified Kramers-Kronig analysis, and measured reflectance shown in Fig. 1 were used to calculate the optical constants shown by the solid lines in Figs. 3 and 4. The dashed lines in these figures indicate the optical constants of fused quartz. It can be seen from these figures that the optical constants of ultrathin silicon oxide film are different from those of fused quartz below the fundamental optical absorption edge of fused quartz. With increasing oxide film thickness,

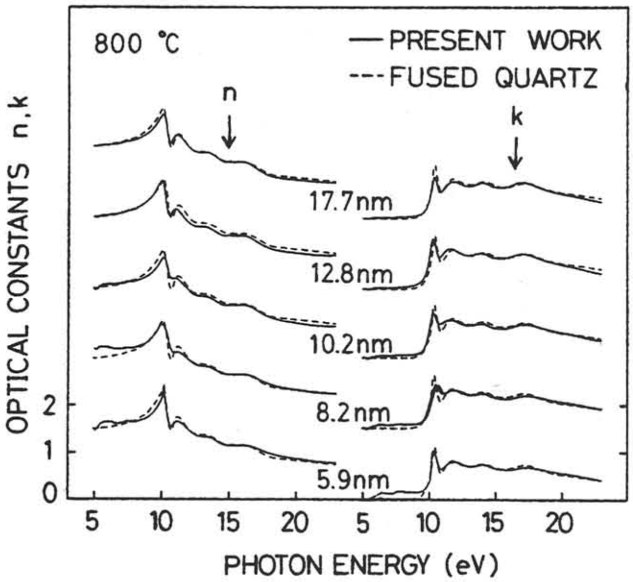

Fig. 3 Photon energy dependence of refractive index and extinction coefficient calculated from reflectance in Fig. 1 for silicon oxide films grown at 800 °C are show by solid lines, while those for fused quartz are shown by dashed lines.

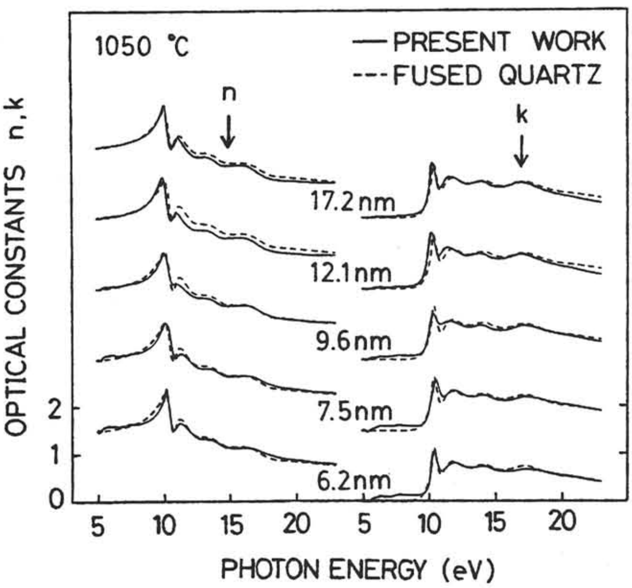

Fig. 4 Photon energy dependence of refractive index and extinction coefficient calculated from reflectance in Fig. 1 for silicon oxide films grown at 1050 °C are show by solid lines, while those for fused quartz are shown by dashed lines.

the optical constants of the silicon oxide film approache to those of fused quartz. The changes in optical properties with the change in oxide film thickness are the same with those obtained for as grown oxide films[1].

The solid lines in Fig. 5 show the photon energy dependence of optical absorption coefficients for oxide films prepared at oxidation temperature of 800 and 1050 °C, while the dashed lines in this figure show that for fused quartz. Therefore, it can be seen from this figure that optical absorption in the oxide film is appreciable below the fundamental optical absorption edge of fused quartz. The increase in optical absorption with decreasing oxide film thickness implies that optical absorption arises from the oxide near the interface. In addition, the increase in optical absorption coefficient at photon energy of 7.8 and 8.6 eV are observed.

The optical absorption tail shown in Fig. 5 can be approximated by exponential

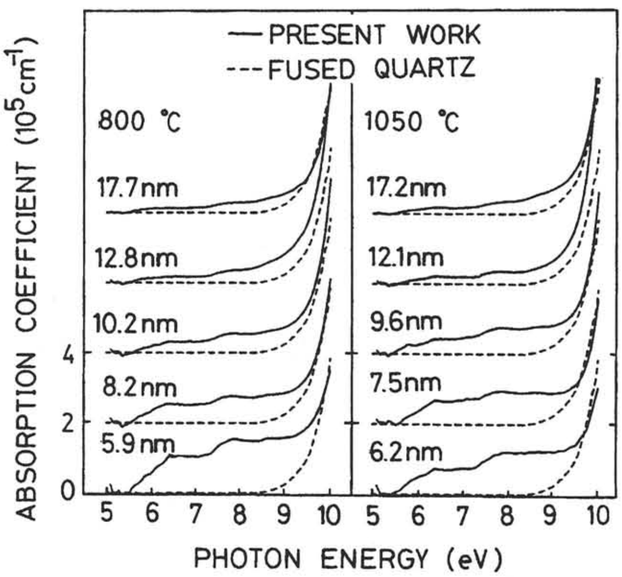

Fig. 5 Photon energy dependence of optical absorption coefficients for oxide films thermally grown at 800 and 1050 °C are shown by solid lines, while that for fused quartz is shown by dashed lines.

decrease, so called Urbach tail. In the following analyses, the optical absorption at 7.8 and 8.6 eV above this optical absorption tail are approximated by the Gaussian function.

From the amount of optical absorption at 7.8 eV in Fig. 5, the amount of Si-Si bond in chemically etched silicon oxide films are evaluated and are shown in Fig. 6. In this figure, the amount of Si-Si bond in as grown oxide films are also shown. Here, the optical absorption cross section determined for Si-Si bond in fused quartz[4] was used. Fig. 6 implies the following: Firstly, the amount of Si-Si bond does not change in the thickness range studied. Therefore, the Si-Si bonds must be located within 6 nm from the interface. Secondly, the amount of Si-Si bond in as grown oxide films are almost the same as those in chemically etched films. Therefore, the Si-Si bonds detected are not produced by the chemical etching. Furthermore, it can be seen from Figs. 2 and 6 that the amount of Si-Si bond are weakly affected by the oxidation temperature. Therefore, the oxide structure producing Si-Si bond are weakly affected by the oxidation temperature.

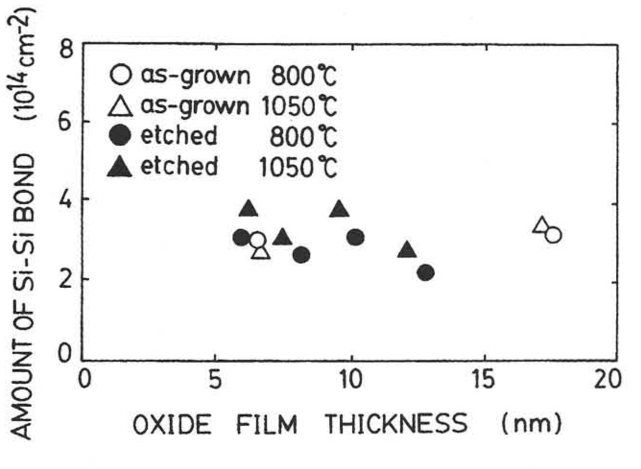

Fig. 6 Amount of Si-Si bond evaluated from optical absorption coefficients in Fig. 5.

5. Conclusion

The change in optical properties of ultrathin silicon oxide films in depth direction were studied. From the analyses of these measurements the optical absorption at photon energy of 7.8 eV were found to arise from Si-Si bonds located within 6 nm from the SiO_2/Si interface. The amount of Si-Si bond are evaluated to be 3×10^{14} cm^{-2}.

References

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