Finding interstitial oxygen in an Si substrate during low temperature plasma oxidation

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Abstract

An Si substrate (100) was oxidized at 400°C in inductively coupled oxygen plasma. Interstitial oxygen was found in the Si substrate at the initial stage of oxidation by IR measurements. An x-ray rocking curve of Si substrates showed a lower peak intensity due to lattice distortion by the interstitial oxygen. The refractive index of thin oxides, below which interstitial oxygen existed in the Si substrate, was smaller than the refractive index of thick oxides, below which no interstitial oxygen existed. The interstitial oxygen was found by plasma oxidation using O_2 gas and N_2O gas. The inductively coupled plasma oxidation using N_2O gas was performed by atomic oxygen, not by molecular oxygen, indicating that atomic oxygen in plasma is responsible for the incorporation of interstitial oxygen.

1. Introduction

Low-temperature silicon dioxide, in which the Si/SiO_2 interface has a good quality, is needed to improve the performance of polycrystalline (poly-) Si thin film transistors (TFTs). Plasma oxidation methods were studied to reduce the temperature of silicon oxidation. Planar-type inductively coupled plasma (ICP) is a high density plasma and the simple structure of the ICP system enables the use of a glass substrate with a large area for low-temperature poly-Si TFTs. ICP oxidation of poly-Si films with O_2 gas improved the performance of the poly-Si TFTs.[1]

ICP with O_2 gas has several active oxygen species in which the kinetics of oxidation growth differs from thermal oxidation.[2] However, not enough attention has been given to the initial stage of ICP O_2 oxidation. In particular, the initial oxidation on an Si substrate is important because carrier mobility is greatly influenced by the surface layer. In this study, we investigated the existence of interstitial oxygen in an Si substrate using ICP oxidation.

2. Experimental

p-type (100) silicon wafers with a boron doping level of $1.5 \times 10^{16}/cm^3$ were used as a substrate. The wafers were cleaned by trichloroethylene, acetone and methanol for 15 min, and by a mixture of boiling sulfuric acid and hydrogen peroxide for 20 min. The wafers were then immersed in a 50:1 HF solution until a hydrophobic surface appeared. The ICP oxidation temperature, power and pressure were 400 °C, 2 kW and 10 mTorr, respectively.

The thickness and refractive index of the oxide were measured by using a Jobin-Yvon ellipsometer. Infrared spectra were obtained using a Nicolet MAGNA-IR 560 FTIR spectrometer with a resolution of 4 cm^{-1} and 32 scans. A background reference sample was obtained after cleaning as just described. An x-ray rocking curve was obtained by using a Bede DCC-300 x-ray diffractometer. The oxygen species in the ICP were monitored by optical emission spectroscopy.

3. Result and discussion

Figure 1a shows the infrared absorption peaks of SiO_2 with various oxide thicknesses, grown at 400 °C in ICP with O_2 gas. The absorption peaks at 1062 cm^{-1} and 817 cm^{-1} are due to the stretching and bending motions of the Si-O bond.[3] The peak at 1106 cm^{-1}, which was due to interstitial oxygen,[4,5] is detected in the oxides with thicknesses of 5.4 nm and 7.8 nm. Figure 1b shows the infrared absorption peaks after oxide etching in a 50:1 HF solution until hydrophobia appears. The absorption peaks at 1062 cm^{-1} and 817 cm^{-1} disappeared because the SiO_2 film was removed. On the other hand, the absorption peak at 1106 cm^{-1} is still detected. This clearly shows that the interstitial oxygen incorporated into the Si substrate in the initial stage of ICP O_2 oxidation. The incorporation of oxygen into the Si substrate might be due to the channeling process when oxygen penetrates through the interstitial sites of Si. Considering the consumption of Si substrate by oxidation, the penetration depth of the interstitial oxygen is about 4 nm.

Figure 2 shows the x-ray rocking curves of Si substrates after oxide etching. The peak intensities of Si substrates, of which 5.4 nm and 7.8 nm oxides were grown and etched, are much lower than the peak intensities of bare Si. The full-width at half maximum (FWHM) of the Si substrates with 5.4 nm and 7.8 nm oxides are 23 arcs and 27.8 arcs, respectively, while that of bare Si is 13.8 arcs. The low peak intensity and large FWHM are due to the distortion of the Si lattice induced by interstitial oxygen. On the other hand, the peak intensities of Si substrates, of which 9.5 nm and 12.3 nm oxides were grown and etched, are similar to that of bare Si. And the FWHM of the Si substrates with 9.5 nm and 12.3 nm oxides are 14.2 arcs and 16.7 arcs, respectively. As the oxide thickness increases, the interstitial oxygen layer of about 4 nm thickness is consumed and the Si lattice distortion decreases.

Figure 3 shows the refractive index of an oxide with various thicknesses for a wavelength of 632.8 nm. The refractive indices of the oxide with thickness of 5.4 nm and 7.8 nm are 1.462 and 1.466, respectively. The refractive index, which is greater than 1.52 when the oxide thickness is greater than 9.5 nm, abruptly increases when the oxide thickness is greater than 9.5 nm. In high-temperature thermal oxidation, the compressively strained oxide with high density grows at the Si/SiO_2 interface due to the volume expansion by oxidation.[6,7] The thermal oxide is then relaxed by the viscoelastic flow of the oxide perpendicular to its surface.[7] The fully relaxed refractive index of thermal SiO_2 is considered to be 1.460.[7] Thin oxides show nearly relaxed refractive indices, while thick oxides with thickness greater than 9.5 nm, are larger than that of thermal oxide. This phenomenon indicates that because the refractive index is a measure of SiO_2 density[6] thick oxides with thickness greater than 9.5 nm have a high density.

In ICP O_2 oxidation, no viscoelastic flow is expected because of its low oxidation temperature. It should be noted that at the initial stage of oxidation, interstitial oxygen distorts the top 4 nm of the Si substrate. Interstitial oxygen enlarges the Si lattice, causing much less compressive stress on the subsequently formed top oxide. Thus, the densification effect, which is caused by compressive stress due to volume expansion, is small for very thin oxides. For thick oxides greater than 9.5 nm, the whole interstitial oxygen layer is consumed, and the volume mismatch between Si and SiO_2 is large. Large compressive stress causes a high-density oxide layer, resulting in an increase of the refractive index. In summary, the expansion of the Si lattice by interstitial oxygen plays a key role in changing the low refractive index for thin oxides.

To understand which oxygen species contributes to the formation of interstitial oxygen, we used an N_2O gas source as well as an O_2 gas source for ICP oxidation. Figure 4 shows the infrared absorption peaks of the ICP oxides grown at 400 °C in the O_2 and N_2O gas sources. The thicknesses of the ICP oxides grown in O_2 gas and N_2O gas are 5.4 nm and 3.8 nm, respectively. Note that the absorption peak at 1106 cm^{-1}, which is due to interstitial oxygen, is most intense. The important point is that the interstitial oxygen layer in the Si substrate can be formed from both gases.

Figure 5 shows the optical emission spectra of plasmas with O_2 and N_2O source gases in the range of 519 nm to 535 nm. In the plasma with the O_2 source gas, the emission line due to O_2^+ ions is observed at 525.1 nm.[8,9] Furthermore, the emission lines due to atomic oxygen are observed at 532.9 nm.[8,9] In the plasma with the N_2O source gas, the emission line due to O_2^+ ions is not detected, while emission lines due to atomic oxygen are observed. This result shows that ICP oxidation with N_2O source gas is mainly performed by atomic oxygen, as in capacitively coupled plasma.[10] Therefore, it can be said that the incorporation of interstitial oxygen into the Si substrate is caused by atomic oxygen, not by molecular oxygen. The existence of the interstitial oxygen layer in Si causes lattice distortion and also, possibly, lattice imperfections. If the thickness of the oxide is less than 10 nm, the interstitial oxygen layer cannot be removed completely. This might cause a large leakage path in semiconductor devices. To avoid a large leakage current by this layer, it is necessary to grow the oxide with a thickness greater than 10 nm. The interstitial oxygen layer should be one of the physical realities of the obscure term "plasma damage".

4. Conclusion

In this study, we have found that interstitial oxygen is incorporated into Si substrates at the initial stage of oxidation at a depth of about 4 nm. The peak intensity of an x-ray rocking curve was strongly reduced due to Si lattice distortion by interstitial oxygen. Thin oxides, below which the interstitial oxygen layer exists, showed a nearly relaxed refractive index in spite of the low oxidation temperature. This was due to less compressive stress on the oxide because the Si lattice was enlarged by interstitial oxygen. The channeling of atomic oxygen caused the incorporation of interstitial oxygen. The formation of the interstitial oxygen layer suggests the oxide thickness should be greater than 10 nm to minimize the current leakage path.

5. Reference

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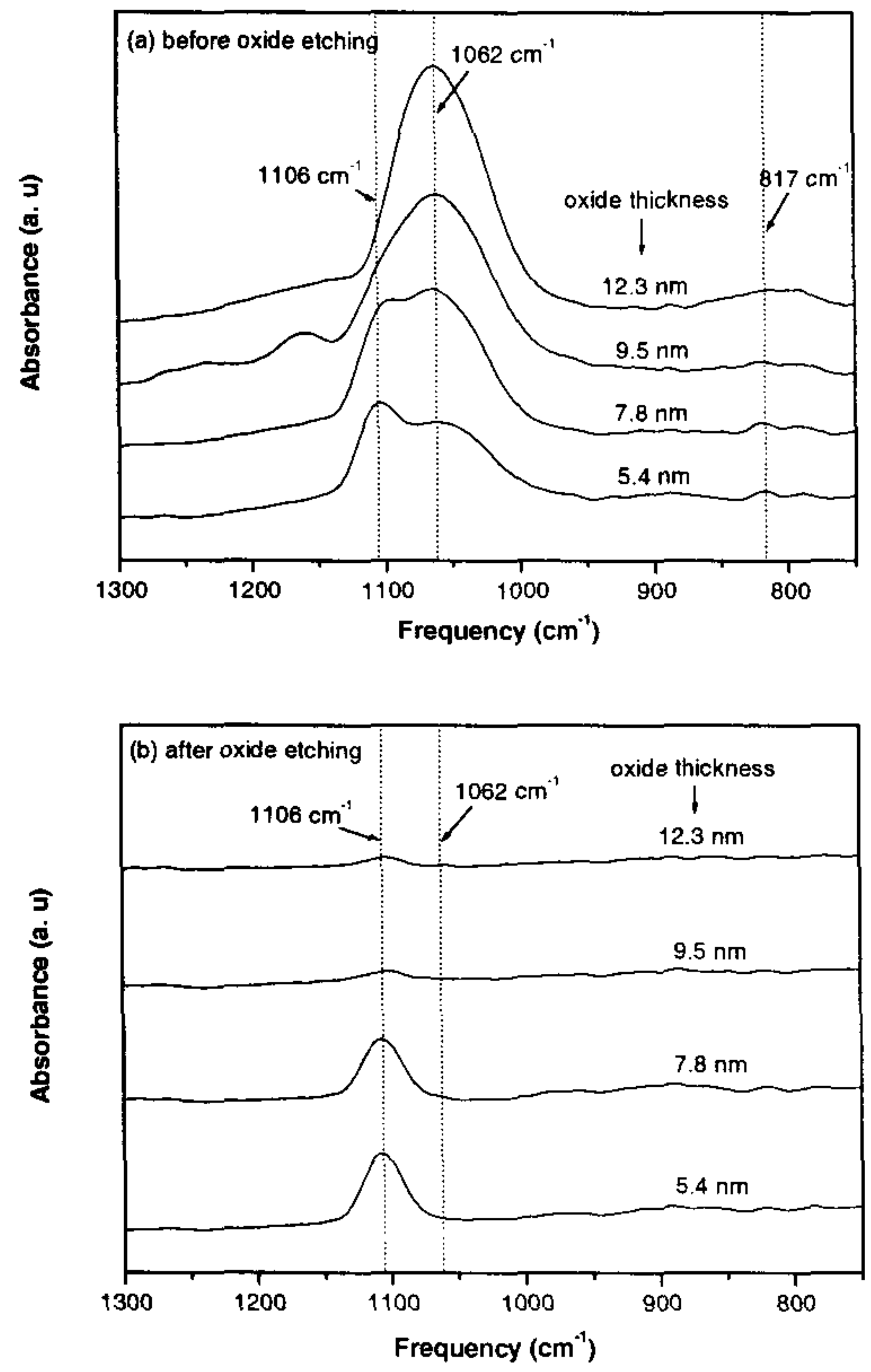

Figure 1. Infrared absorption spectra of SiO$_2$: (a) before etching; (b) after etching with various oxide thicknesses

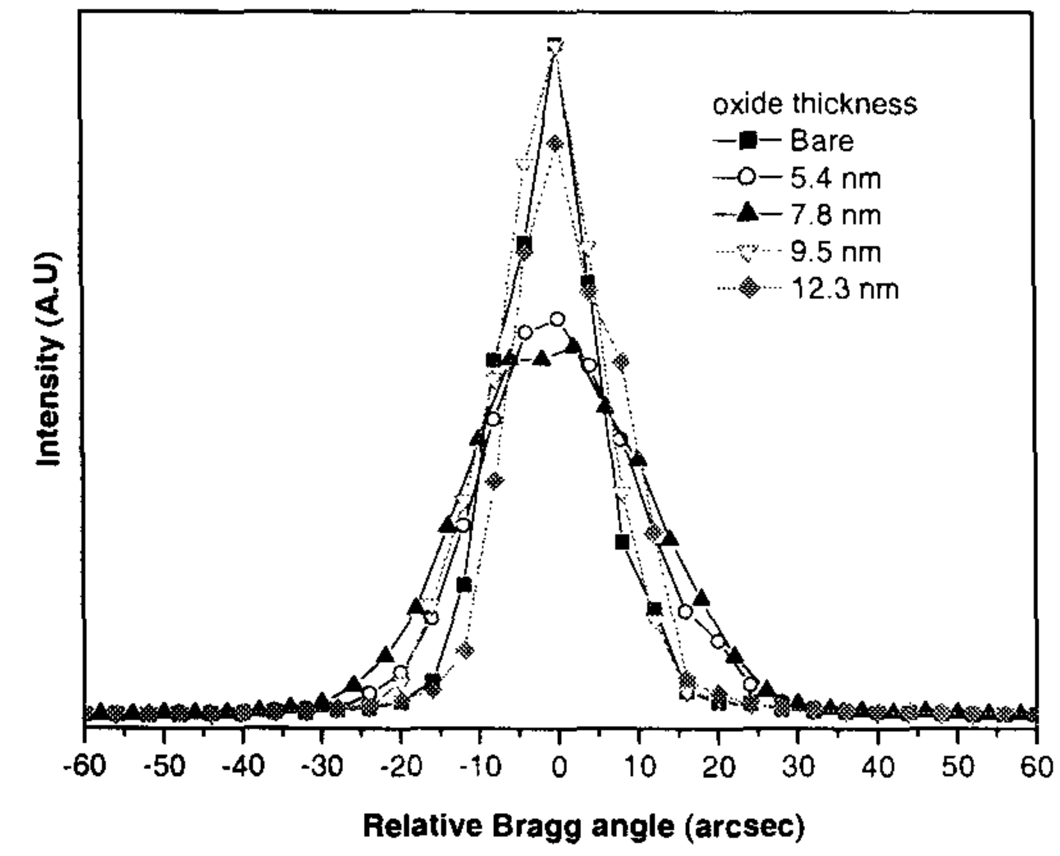

Figure 2. X-ray rocking curves of the Si substrates after oxide etch

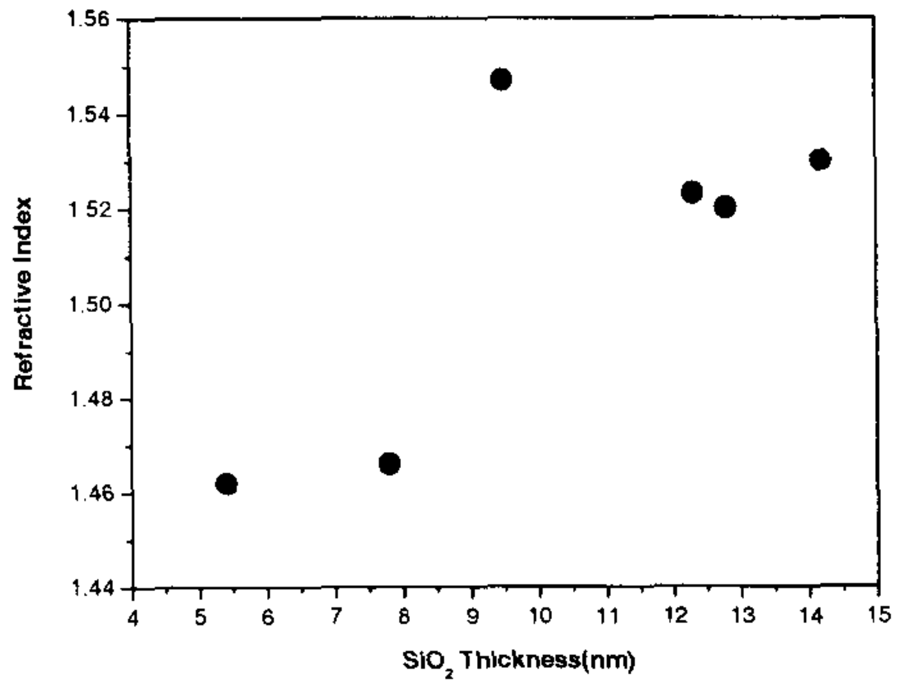

Figure 3. Refractive index as a function of oxide thickness

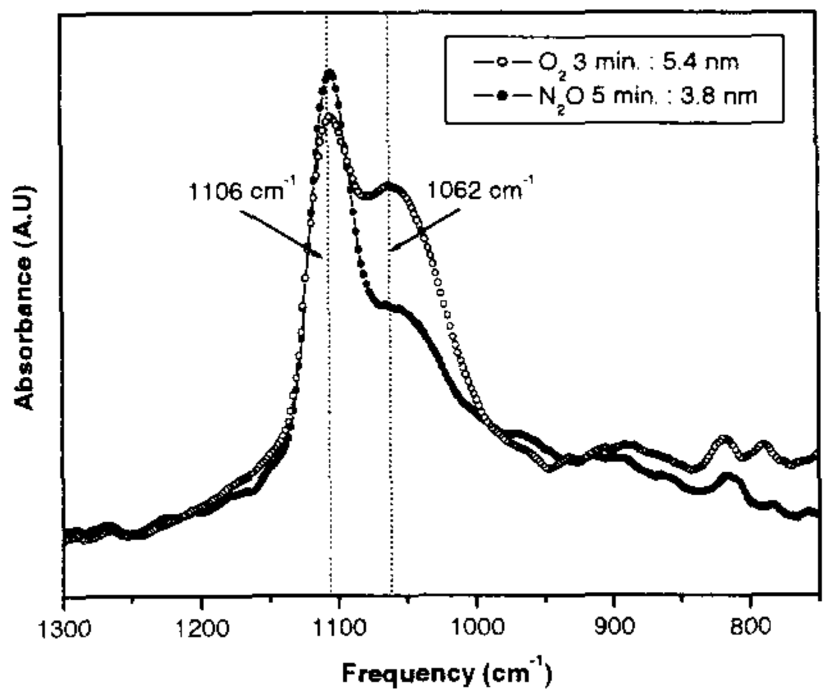

Figure 4. Infrared absorption spectra of ICP oxides grown at 400 °C in O$_2$ gas and N$_2$O gas

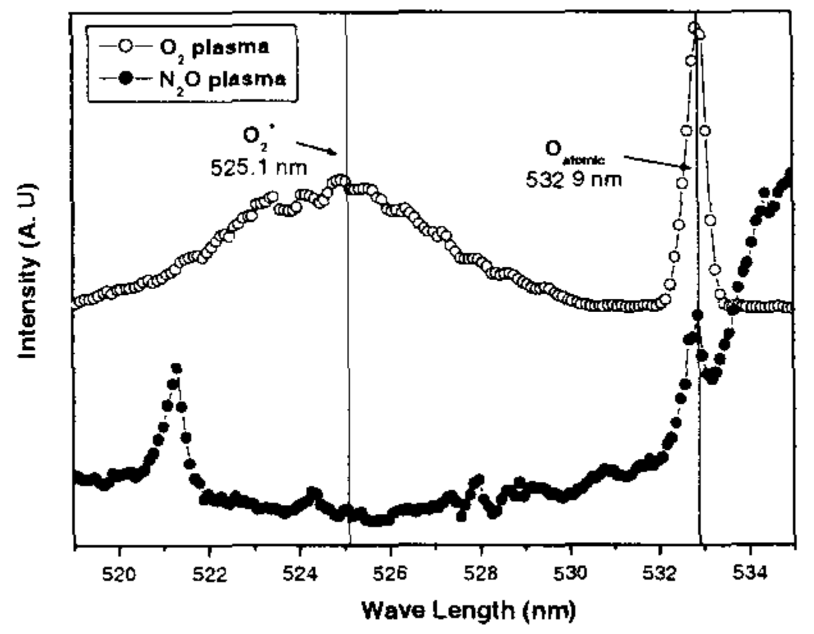

Figure 5. Optical emission spectra of plasmas with O$_2$ and N$_2$O gas sources, in the ranges of 519 nm to 535 nm