

Phosphorous Incorporation in Ultrathin Gate Oxides and Its Impact to the Network Structure

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1. Introduction

The dielectric degradation of gate oxides thinner than 5nm has been associated with the existence of compressively-strained SiO₂ bonds near the SiO₂/Si interface [1]. Impurity redistributions [2] in the poly-Si gate/SiO₂/Si system during device fabrication process as well as influence of diffused impurities in SiO₂ on the network structure and built-in stress near the SiO₂/Si interface are thought to be crucial for developing a gate oxide wear-out model.

In this paper, we have demonstrated heavy incorporation of phosphorus atoms in ultrathin gate oxides during n⁺-poly Si gate formation process. The resulting structural relaxation in the SiO₂ network and chemical states of phosphorus atoms have been studied by high-resolution x-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared attenuated total reflection (FT-IR-ATR) spectroscopy.

2. Experimental

Ultrathin gate oxides were grown at 900°C in dry O₂ on p-type Si(100) and subsequently 200nm-thick undoped poly-Si was deposited at 640°C by low-pressure CVD from SiH₄. The phosphorous diffusion utilizing POCl₃ was carried out at 900°C for 10min followed by 900°C annealing for 10min. Depth analysis of the phosphorous incorporation and the chemical structure for the oxide layer was performed by measuring XPS spectra of P_{2p} and Si_{2p} core levels and p-polarized ATR spectra, respectively, at each step of SiO₂-thinning by dilute HF etching.

3. Results and Discussion

The concentration of phosphorous atoms incorporated in the oxide is higher than that in poly-Si bulk layer ($\sim 2 \times 10^{20} \text{cm}^{-3}$) as shown in Fig. 1. It is also confirmed that phosphorous pile-up at the poly-Si/SiO₂ interface is as high as 10^{21}cm^{-3} in the poly-Si layer within $\sim 5 \text{nm}$ from the interface. Thus, P atoms diffuse into the SiO₂ layer and again pile up in the region within $\sim 1.5 \text{nm}$ from the SiO₂/Si(100) interface. This pile-up might be promoted by the existence of strained Si-O-Si bonds in SiO₂ near the interface. In fact, the IR absorption peak of the LO phonon mode for Si-O-Si lattice vibrations observed in ATR spectra for as-grown oxides thinner than 2nm shifts toward the lower wavenumber by $\sim 30 \text{cm}^{-1}$ as oxide thickness decreases down to 0.6nm [3], indicating

that the compressively-strained SiO₂ network is formed near the SiO₂/Si(100) interface as represented in Fig. 2. It is likely that the built-in compressive stress near the interface is reduced by phosphorous incorporation, being consistent with the fact that the etch rate of the P-diffused oxide in a 0.1%HF solution is constant independent of the oxide thickness, while that of the pure oxide is reduced in the thickness range below $\sim 1.5 \text{nm}$ as indicated in Fig. 3. To get an insight on the structural relaxation for P-diffused oxides, the chemical bonding features of phosphorous atoms in the oxide were examined by transmission IR and XPS. The infrared absorptions due to the stretching and the bending vibrational mode of three-fold coordinated P=O double bonds at $\sim 1310 \text{cm}^{-1}$ and $\sim 800 \text{cm}^{-1}$, respectively, are observed for P-diffused oxides as in the case of phosphosilicate glass (PSG) as shown in Fig. 4. Furthermore, P_{2p(3/2)} XPS spectra for the P-diffused oxides can be deconvoluted into five components as demonstrated in Fig. 5. Taking into account the local electronegativity for phosphorous atom including the first and the second nearest-neighbor atoms, it is found that three- and four-fold coordinated P atoms coexist at the SiO₂/Si(100) interface and in bulk SiO₂. Therefore, the incorporation of three-fold coordinated P in the oxide network is considered to induce the structural relaxation of the strained bonds near the interface.

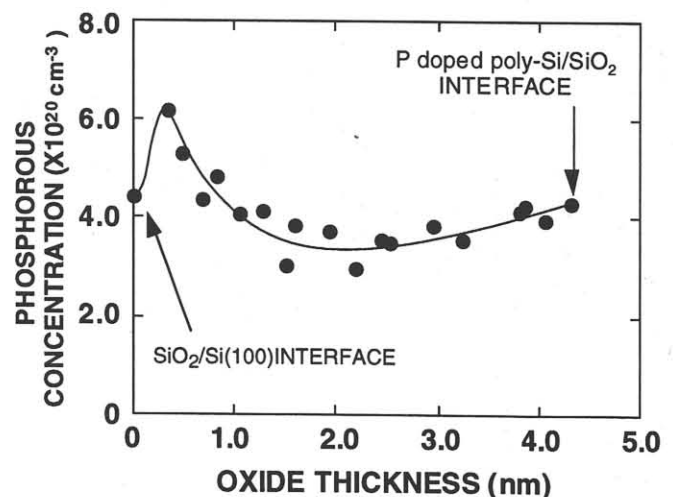


Fig. 1 Phosphorus concentration profile in a 4.3nm-thick gate oxide as determined by P_{2p} core level signal intensity with step-by-step oxide stripping. Very homogeneous oxide etch is confirmed by AFM.

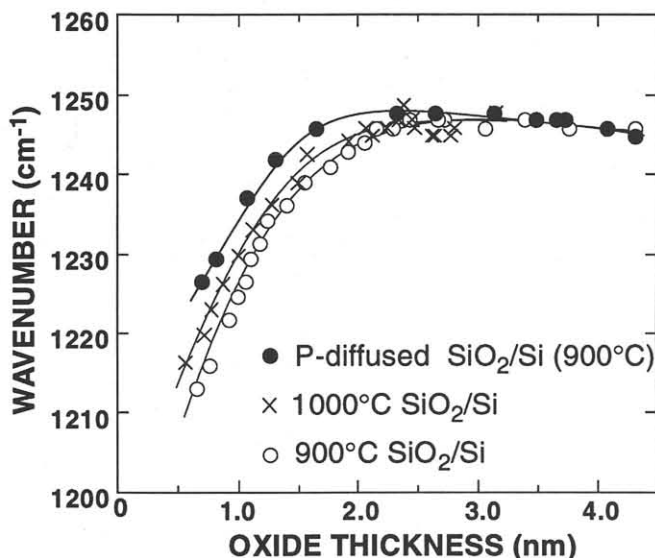


Fig. 2 The absorption peak of LO phonon mode as a function of oxide thickness for P-diffused and pure oxide grown on Si(100) wafers at 900 or 1000°C.

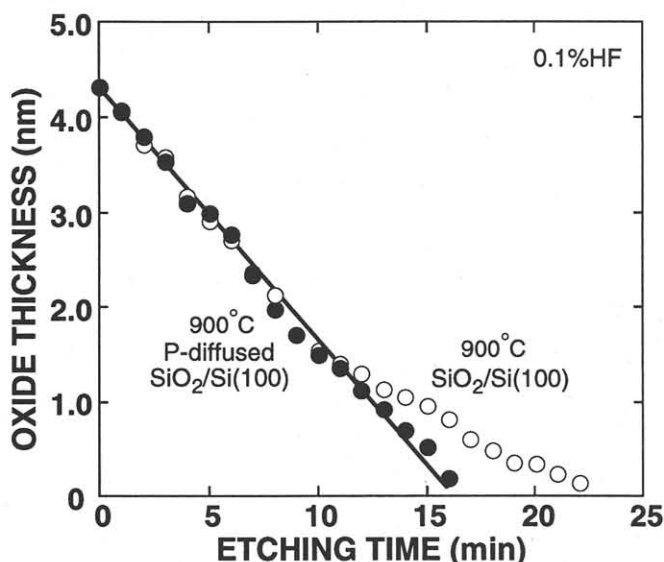


Fig. 3 The oxide thickness as a function of etching time in a 0.1% HF solution. P-diffused and pure oxide prepared at 900°C were simultaneously etched in the same HF solution.

The valence band offset for the P-diffused SiO₂/Si(100) interface is determined to be 4.55±0.1eV by a spectral deconvolution of a measured valence band spectrum into the spectra originating from the oxide layer and underlying Si(100), being almost identical to that for pure SiO₂/Si(100) [4]. Also there is no observable difference in the SiO₂ bandgap (8.9 ~ 9.0eV) determined from the onset of the energy loss spectrum of O_{1s} photoelectrons for the P-diffused and pure oxides [3].

4. Conclusions

Surprisingly high concentration of phosphorous atoms is incorporated in ultrathin gate oxides as confirmed by high resolution XPS. Three-fold coordinated atoms relax the built-in compressive stress in the oxide layer near the

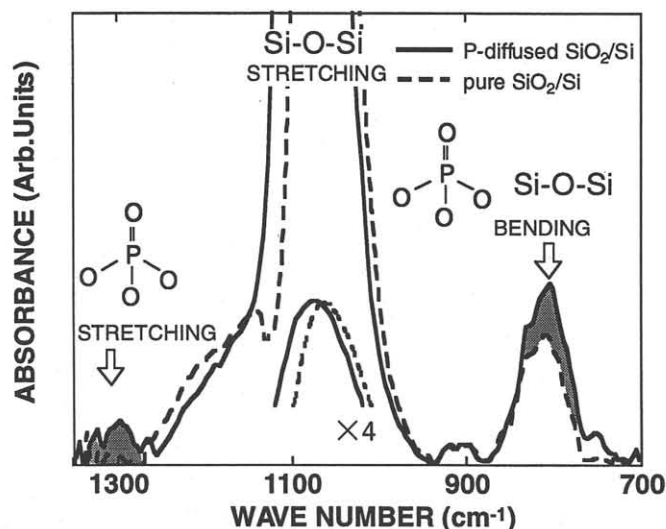


Fig. 4 Transmission IR spectra for 4.3nm-thick P-diffused and pure oxides grown on Si(100) at 900°C

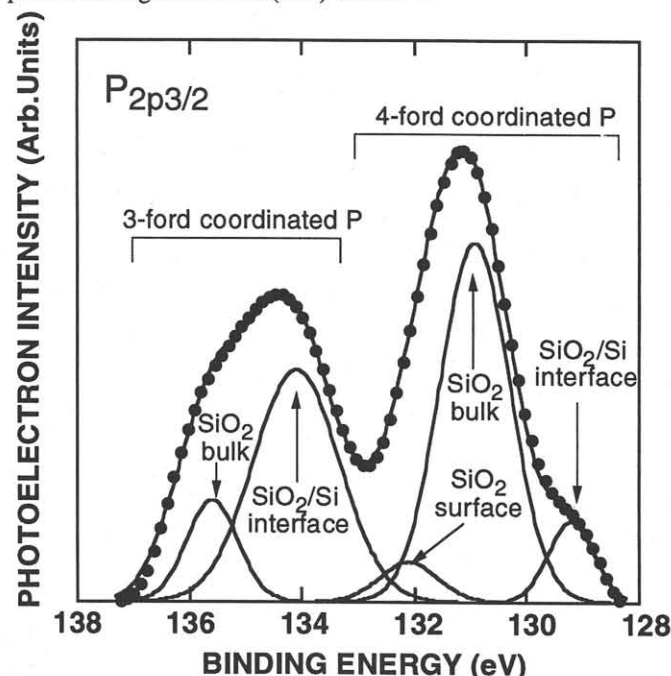


Fig. 5 A high-resolution P_{2p(3/2)} spectrum for P-diffused oxide etched-back to 1.9nm in thickness and the deconvoluted spectra.

SiO₂/Si(100) interface.

Acknowledgments

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References

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