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Stress Field Dependence of the Silicon Oxidation Rate

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We have investigated the effect of mechanical stress on the chemical oxidation process of Si with a newly developed technique to induce uniform uniaxial stress. We have found that the precise control of curvature of the Si wafer is essentially important to achieve uniform stress. XPS measurements have revealed that the effect of the stress field on the growth rate for the chemical oxides is smaller than that for the thermal oxide. It has been also found that stress during the chemical oxidation does not affect the electronic states of chemical oxide.

Keywords: mechanical stress, silicon oxides, oxidation rate, XPS, XANES

1. INTRODUCTION

With the scaling down of Si-ULSIs, detrimental effects of the mechanical stress on the characteristics of MOS transistors have become prominent. For example, it is well known that the mechanical stress enhances the leakage currents at the local oxidation of silicon (LOCOS) edge. [1] Furthermore, Takahashi et al.[2] reported the successful formation of single electron transistor (SET) taking advantage of stress-induced enhanced oxidation and named PADOX (Pattern-dependent oxidation). In spite of its importance, the effect of the stress field on the Si process chemistry has not been well understood yet. The lack of basic understanding is mainly due to the difficulty in the control of stress field. For example, Tamura et al. showed that the growth rate for the thermal oxidation strongly depends upon the stress field. However, they induced stress in the Si wafer by the conventional three point bending method in which the wafer is bent by the force from the tip of the screws. It should be noted that the stress induced by this method varies from 0 Pa to the maximum value in the sample. As a result, the oxidation rate depends strongly on the position in the wafer.

The scaling of Si-ULSIs in the lateral direction has also requested the reduction in the gate oxide thickness. In fact, n channel MOS transistors with a gate oxide thickness as thin as 15Å were fabricated and found to be promising for future VLSIs in spite of the large leakage currents through the gate oxide.[3] This thickness is almost equivalent to that of the chemical oxide which is formed in the wet solution to protect the Si surface just before the thermal oxidation process in the furnace. Hence, the quality of the chemical oxide has become increasingly important. To the best of our knowledge, there has been no report which dealt with the stress dependence of the growth rate for the chemical oxide.

In the present work, we point out the importance of the control in the curvature of the Si wafer to obtain homogeneous stress and report the effect of the mechanical stress on the chemical oxidation process of Si.

2.EXPERIMENTAL

The mechanical stress was imposed on a Si wafer using the sample holder as shown in Fig.1. With this holder, Si wafers are sandwiched between two parts and bent with a constant curvature, which is essentially important to obtain homogeneous uniaxial stress. The radius of the cylindrical holder is 15mm. We found that the use of a conventional Si wafer with a thickness around 0.5mm is not appropriate for this purpose because of its brittleness. We solved this problem by the use of the flexible Si wafer with a thickness less than 50 μ m.

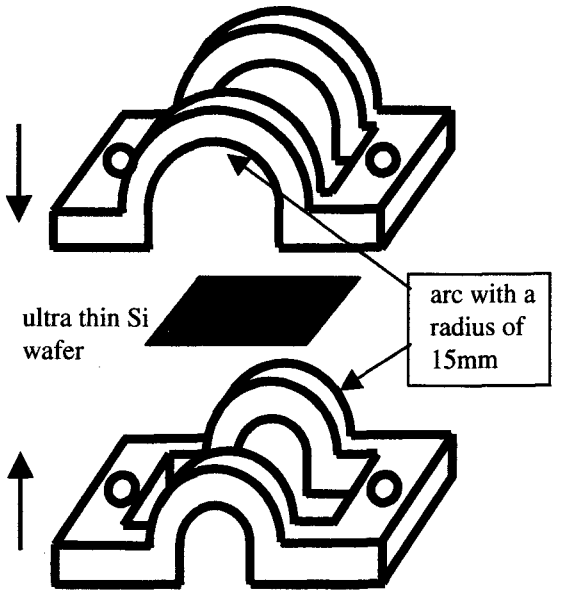

Fig.1. Schematic diagram of the sample holder to obtain homogeneous uniaxial stress.

Table I Conditions for the chemical oxidation

wafer thickness	chemicals	temperature	oxidation time
14 μ m	HNO_3	90℃	30minutes
14 μ m	HNO_3	90℃	5minutes
14 μ m	HNO_3	90℃	2minutes
32 μ m	HNO_3	90℃	30minutes
32 μ m	HNO_3	90℃	5minutes
32 μ m	H_2SO_4:H_2O =1:1	90℃	5minutes
32 μ m	H_2SO_4:H_2O =1:1	90℃	30seconds
32 μ m	HCl:H_2O_2:H_2O =3:3:5	70℃	5minutes

Using the sample holder described above, we have investigated the effect of mechanical stress on the chemical oxidation processes. Firstly, a thin Si wafer bent in the sample holder was immersed in a hydrofluoric acid solution to remove the native oxide. After rinsing in a deionized water, we performed chemical oxidation under various conditions. Table I summarizes the conditions for these chemical oxidation processes. After the oxidation, the samples were taken out of the holder and cut into two pieces to investigate the oxidation rate for the compressed surface and the dilated surface. Since the two samples were put in the XPS chamber simultaneously, we can reduce the experimental error which stems from the oxidation during the sample transfer from the sink to the XPS chamber. The XPS measurements are performed using VG ESCALAB MK II with an X-ray source of Mg K α ($h\nu$ =1253.6eV) and Al K α ($h\nu$ =1486.6eV). The angle between the sample normal and the detector was set at 15° .

We also performed Si K-edge X-ray absorption near edge structure (XANES) measurements to investigate the electronic structure in the conduction band. For the XANES experiments, we used the synchrotron X-ray source monochromatized with InSb (111) crystals at BL-27A in the KEK-PF. Since the thicknesses of our samples were thin, we used the total electron yield method to obtain absorption spectra which is sensitive to the surface.

3. RESULTS AND DISCUSSIONS

3.1 Analysis of stress distribution

We have compared the stress distribution in our sample with that formed by the conventional three point contact method. To obtain stress distribution, we must know the shape of the wafer which can be calculated with the Castigliano's theorem:

$$\frac{\partial U}{\partial W_j} = v_j \quad \ldots(1)$$

where U is the elastic energy of the sample, W_j is the load for the j-th element, and v_j is the deflection for the j-th element.

The radius of curvature can be estimated from the shape of the wafer. Using the radius, the stress distribution can be calculated with the following equation:

$$\sigma_{(\rho)} = \frac{E}{\rho} y \quad \ldots(2)$$

where σ is the stress, E is Young's modulus, ρ is the radius of curvature, y is the distance from the neutral surface.

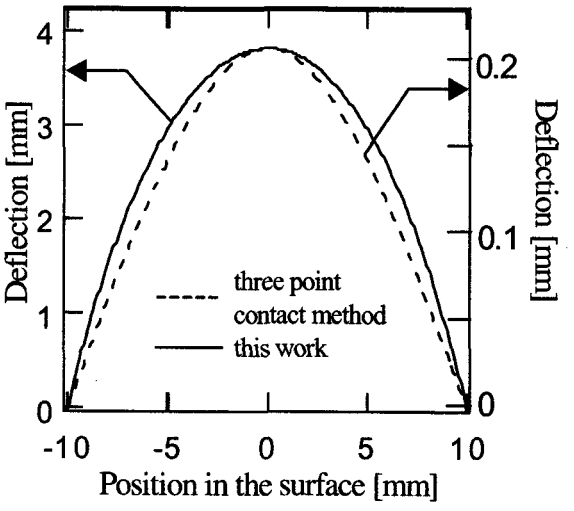

Fig. 2. The deflection of the wafer surfaces by the three point contact method and the newly developed method.
Three point contact method : The thickness of the wafer is 0.5mm and the stress is 100MPa at the center of the sample.
This work : The thickness of the wafer is 14 μm and the radius of curvature is 15mm.

Figure 2 compares the shape of the wafers bent by the three point contact method and the newly proposed method. Note that the radius of the sample bent by the three point contact method is very large at the end of the sample, which in turn leads to the weak stress at the wafer edge. In fact, the mechanical stress at the Si surface calculated with Eq. (2) varied from 0Pa at the edge to 100MPa at the center. On the contrary, a constant radius can be seen for the sample bent with the new sample holder which corresponds to the uniform stress.

The uniaxial stresses at the surface for the wafers bent in the new sample holder with the wafer thicknesses of 14 μm and 32 μm are calculated to be 61MPa and 140MPa, respectively.

3.2 Effect of stress on chemical oxidation

For the estimation of the oxide thickness, we used Si 2*p* XPS spectra. Figure 3 shows a typical Si 2*p* spectrum for the Si wafer oxidized in the HNO_3 solution. The main peak and the shoulder at the higher binding energy can be attributed to the bulk Si and the oxide on the surface, respectively. We deconvoluted the peak into the two components with the mixed function of the Gaussian and the Lorentzian and calculated the area for each component. Theoretically, the integrated peak intensities of Si 2*p* for the the SiO_2 film, $I_{Si2p}(SiO_2)$, and substrate,

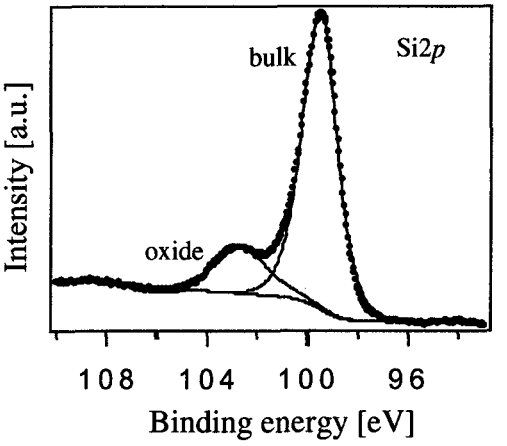

Fig. 3. A typical Si 2p XPS spectrum for the Si wafer oxidized in the HNO_3 solution. The dotted line is the spectrum and the solid line is the result of the curve fitting.

I_{Si2p}(bulk), should be given by;

$$I_{Si2p}(SiO_2) = k\int_0^d n_{SiO_2}\sigma_{Si2p}\exp\left(-\frac{z}{\lambda_{SiO_2}\cos\theta}\right)dz \quad \ldots(3)$$

and

$$I_{Si2p}(bulk) = k\int_0^\infty n_{Si}\sigma_{Si2p}\exp\left(-\frac{z}{\lambda_{Si}\cos\theta}\right)dz\cdot\exp\left(-\frac{d}{\lambda_{SiO_2}\cos\theta}\right) \ldots(4)$$

where, σ_{Si2p} is the photoionization cross section, λ_{Si}(= λ_{SiO2}) is the escape depth of the photoelectrons, k is a constant, d is the oxide thickness, z is the depth, θ is the take-off angle of photoelectrons, n_{SiO2}=1/3, and n_{Si}=1.

From the Eq. (3) and the Eq. (4), we have derived the equation for the determination of the oxide thickness as:

$$\frac{I_{Si2p}(SiO_2)}{I_{Si2p}(bulk)} = \frac{1-\exp\left(-\frac{d}{\lambda_{SiO_2}\cos\theta}\right)}{3\exp\left(-\frac{d}{\lambda_{Si}\cos\theta}\right)} \quad \ldots(5)$$

Figure 4 shows the ratio of oxidation rate for the dilated surface to that for the compressed surface in various wet solutions. As can be seen in this figure, the growth rate ratio is close to the unity for all the solutions. Tamura et al. reported that compressed Si surfaces show an increased thermal oxidation rate for the oxide

thickness less than 3nm and a reduced rate for oxide

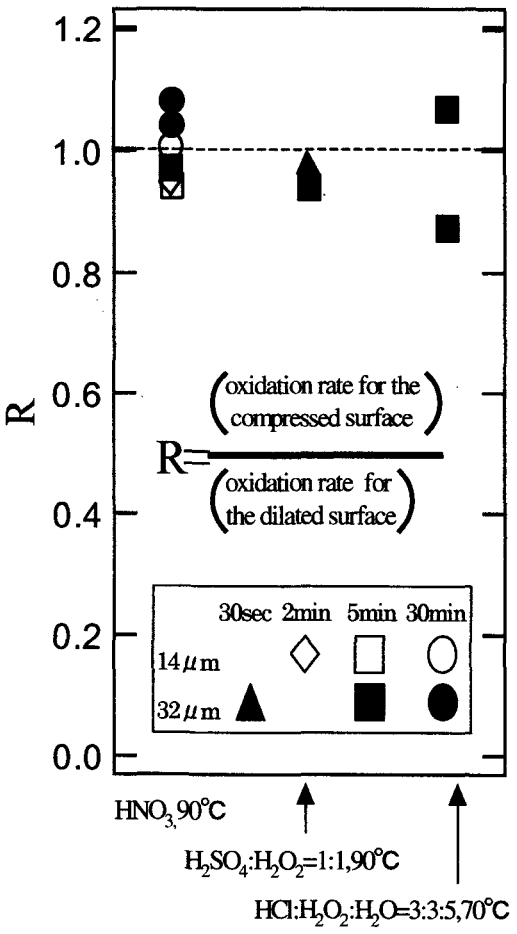

Fig. 4. The ratio of oxidation rate for the dilated surface to that for the compressed surface in various wet solutions.

thicker than 3 nm.[4] Their report makes a clear contrast with our experimental result on the chemical oxidation in which there is only small stress dependence in the oxidation rate. At present stage, we attribute this to the low density of the chemical oxide[5], in which stress dependence of the diffusivity for the active species of the oxidation is expected to be small.

The electronic states of the oxide have been studied with XANES and XPS. It has turned out that the Si K-edge XANES spectra of the sample oxidized under compressive and tensile stress in HNO_3 are quite similar. Since the K-edge XANES spectrum corresponds to the p-like empty states, this result indicates that the electronic states in the conduction band of the chemical oxide are not seriously affected by the stress during the oxidation. Similar results have been obtained for XPS spectra for samples oxidized under compressive and tensile stress in HNO_3. The XPS spectra should include information on the valence band of the oxide. These results indicate that electronic states of chemical oxide both in the conduction band and the valence band is not very sensitive to the stress during the growth.

4.CONCLUSIONS

We have succeeded in inducing uniform uniaxial stress on Si wafers using a newly developed technique in which the curvature of the wafer is kept constant. XPS measurements have revealed that the effect of stress field on the growth rate for the chemical oxides is smaller than that for the thermal oxide. It has been also found that the electric states of the chemical oxide is not sensitive to the stress during the growth.

5.ACKNOWLEDGEMENT

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