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A Measurement of the Effect of Intrinsic Film Stress on the Overall Rate of Thermal Oxidation of Silicon

by

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The effects of intrinsic film stress on Si oxidation kinetics has been receiving considerable attention in recent years(1-5). Oxidation models have appeared that relate the Si-SiO_2 interfacial intrinsic stress to both the interface reaction between oxidant and Si and to a stress altered oxidant transport. The experimental measurement of the film stress itself has been reported, although to date the data is rather sparse(1,6). Recently, in our laboratory more extensive intrinsic stress measurements have been made and these measurements will be reported separately. So while the existence of a compressive intrinsic SiO_2 film stress has been experimentally verified, the experimental verification of the effects of the stress on oxidation kinetics remains a matter of speculation within the various models.

Along with the development of an intrinsic film stress due to the molar volume change during the oxidation of Si, a SiO_2 film density increase occurs and has been measured (6, 10, 11). The density increase of 2-3% is too large to have arisen from the stress optical constant and has therefore been attributed an accomodation of system to the buildup of stress (6). We consider the intrinsic stress and density increases to have a common origin in the nature of the Si oxidation process on a single crystal Si surface. The present communication provides a rather direct experimental measurement of the effect of the compressive intrinsic film stress and/or oxide density on the Si oxidation kinetics.

We report the result of a simple but careful experiment that shows the parallel between stress and/or density and kinetics in the thicker film regime of Si oxidation where the film thickness, L, is greater than 100nm, and at an oxidation temperature of 800°C. In this thickness range, the transport and interfacial effects are nearly equivalent. The results show a decrease in the rate of oxidation as had been anticipated for a compressive stress and/or for a higher density film.

EXPERIMENTAL PROCEDURES

All the Si wafers used were lightly P doped n-type (100) oriented commercially available high quality single crystal Si slices. The wafers were cleaned by a slightly modified RCA procedure(7) and followed with an HF dip and thorough deionized H_2O rinse. A batch of ten wafers was oxidized in pure dry O_2 at 800°C to an oxide thickness of between 100-110nm. This thickness was chosen to be near a half of an ellipsometric period (about 140nm for 632.8 nm light) so that both SiO_2 film thickness and refractive index could be accurately measured. The batch was then split in half with one half receiving a one hour 1000°C anneal in pure Ar so as to relieve the stress. This anneal was found to be more than adequate for this purpose(6). At this point all the wafers were measured by ellipsometry. The ellipsometer was of research quality with the capability of polarizer and analyzer resolution to 0.01° and was carefully aligned prior to use. The Δ and Ψ values were converted to SiO_2 thickness and refractive index using a modified version of McCrackin's program(8). We conservatively estimate a thickness and index accuracy of better than 2% and 0.005, respectively. The batch halves were recombined and then the entire batch was oxidized at $800^{o}C$ in pure O_2. Wafers were selected from each half batch (the annealed and unannealed halves) at various oxidation times so that film thickness and refractive indices could be remeasured.

EXPERIMENTAL RESULTS AND DISCUSSION

Table 1 shows a comparison of the film thicknesses and refractive indices after the final $800^{o}C$ oxidation for the oxidation time noted in the left most column. The SiO_2 film thickness is reported as the difference between the initial $800^{o}C$ oxidation to produce the 100-110nm samples and the final oxidation at $800^{o}C$ to compare the unannealed and annealed samples. In all cases the stress annealed samples grew oxide more rapidly than the stressed samples. The refractive indices indicate that the unannealed samples had the higher density and stress throughout the final oxidation as had been previously reported (6).

Within the Deal and Grove model(9) the transport of oxidant is governed by the parabolic rate constant, k_p and is given as:

$$k_p = 2CD/\rho \qquad [1]$$

where C is the dissolved oxidant in SiO_2, D is the oxidant diffusivity and ρ is the SiO_2 density. The transport term can then be reduced by either a decrease in D or an increase in ρ or both. Recently, several studies have shown the likelihood of the intrinsic compressive SiO_2 film stress decreasing D (4,5). Also several studies have shown that the oxide density, ρ, increases with decreasing oxidation temperature(10,11). The experiments reported herein cannot distinguish between these two factors, as both stress and density increase with decreasing oxidation temperature and both anneal out with high temperature treatment (6).

For the interface reaction, a revised formulation now includes the effect of film stress and oxide viscosity (3, 6). In this model (12), the interface reaction constant k_1 is given as:

$$k_1 = kC_oC_{Si}\sigma/\eta \qquad [2]$$

where k is a constant, C_o and C_{Si} are the oxygen and silicon concentrations, σ is the intrinsic stress and η is the viscosity of SiO_2. The compressive SiO_2 stress is tensile in Si thereby stretching the Si - Si bonds and increasing the likelihood for oxidation. At low temperatures σ is larger (1, 6) but so is η hence we can neither distinguish σ from η effects nor k_1 from k_p effects. Despite these difficulties, we have demonstrated that the overall rate of oxidation of Si is reduced in low temperature grown thermal oxide films on Si, and the reduction is linked to the intrinsic film stress. At the present time, more detailed studies aimed at separating film stress and density effects are in progress in our laboratory.

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Table I

SiO_2 Film Thickness and Refractive Index
Comparsion for Annealed and Unannealed Samples

Oxidation Time of Second Oxidation (hrs.)	Unannealed		Annealed	
	Thickness (Å)	Ref. Index	Thickness (Å)	Ref. Index
1	9	1.474	23	1.463
2	15	1.475	44	1.465
4	30	1.475	83	1.465
9	78	1.474	163	1.466
19	178	1.473	267	1.466