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IN-SITU STRESS MEASUREMENTS DURING
THERMAL OXIDATION OF SILICON

by

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In-Situ Stress Measurements During

Thermal Oxidation of Silicon

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Abstract

A two beam laser reflection technique was used to measure SiO_2 film stress during Si oxidation, i.e. in-situ at the growth temperature. Results show a higher compressive intrinsic film stress near the Si- SiO_2 interface and a lower stress in the bulk of the SiO_2 film. Thermal stress is also measured by monitoring the SiO_2 film covered Si substrate curvature changes during temperature excursions. Our new results are in general agreement with previous ex-situ stress measurements and may indicate that film stress, being highest at the interface, influences the interface reaction in Si oxidation.

Introduction

The advent of smaller and faster MOS devices has facilitated the need for thinner gate oxides ($<200\text{\AA}$) and lower process temperatures ($<900^\circ\text{C}$). These requirements constrain Si oxidation kinetics to a region which is not well described by the currently accepted linear-parabolic oxidation model (1). In particular, this model does not explain the anomalously high oxidation rates observed in the early stages of oxidation (1-4).

A number of studies have reported the observation of film stress as a result of Si oxidation (5-8). An intrinsic stress, σ_i , originates from the molar volume change when converting Si to SiO_2 , and a thermal expansion stress, σ_{th} , arises from the thermal contraction mismatch which results upon cooldown from oxidation. The intrinsic stress increases with decreasing oxidation temperature, and thus will be even more important for future device fabrication at lower temperatures. Usually the total residual stress, $\sigma_i + \sigma_{th}$, is measured at room temperature. However, as will be shown below, the in-situ stress measurement under oxidation conditions enables the uncoupling of the total stress into the two components. There are differing views on how stress may affect oxidation. Some models consider how stress alters the interface reaction (9-12) while others focus on effects on the stress altered transport of oxidant through the oxide (13-15).



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We report new experimental results on film stress measured both at the oxidation temperature during film growth and upon cooling to room temperature. These results show initially high intrinsic film stress which undergoes relaxation as oxidation proceeds. Our results are discussed in terms of a contribution to the interface reaction at the Si-SiO₂ interface, since the stress is highest at this position and available data indicates that this process is more important than diffusion in the very early stages of Si oxidation (16). We also report the measurement of thermal stress during thermal cycling, and obtain experimental values for the elastic constants of SiO₂.

Experimental Procedures

All film stress measurements were carried out using commercially available p-type, 2 Ω -cm, (100) Si wafers which were 5 cm in diameter and 75 μ m thick, but which were cleaved to form $\sim 3 \times 4$ cm samples. Prior to cleaving, the original wafers received a pre-oxidation at 1000°C to prevent any contamination from Si dust as a result of scribing. After removal of this protective oxide in concentrated HF, the samples were cleaned using a modified RCA method (17) prior to final experimental oxidations.

Stress measurements at the oxidation temperature were performed using a modification of the laser reflection technique previously reported (8). The modified apparatus is depicted in Figure 1. The essential elements include a plate type beamsplitter (BS1) which splits light from a He-Ne laser (6328Å)

into two orthogonal beams which are made parallel by aligning the mirrors (M1 and M2) and the reflecting prism. The beams are transmitted through a second beamsplitter (BS2) and reflected into an oxidation furnace using the mirror M3. After reflecting from the sample, the beams return to M3 and are reflected to a larger flat mirror M4 by the beamsplitter BS2 to increase the reflection path length and hence the measurement sensitivity. The beams are then returned to a measurement screen to determine the separation distance which can be used to calculate the wafer curvature (8). If oxidation results in warpage of the Si wafer, then a deviation in the initial separation of the beams is observed. Calibration procedures were previously described (8).

The oxidation furnace, which was placed in the path of the parallel light beams in the stress measurement apparatus, consisted of a resistively heated fused silica tube. A constant flow of gaseous N_2 taken from a liquid N_2 source was maintained inside the furnace except during oxidation where ultra high purity O_2 (less than 1 ppm H_2O and 0.5 ppm hydrocarbons) was used. All furnace components were constructed of fused silica. All temperatures are reported with a variation of $\sim 3^\circ C$, which is attributed to the small size of the hot zone. The water content inside the furnace was monitored constantly in the effluent gas using a capacitance hygrometer. Figure 1 also includes an H_2O fused silica bubbler which was connected in series with the gas feed line to clean the furnace between runs, and which is followed by extensive drying in N_2 before experimental runs. The furnace

endcap had an optically flat strain-annealed pyrex window to allow entrance and exit of the laser beams without deviation or significant absorption loss.

To allow for easier sample alignment, a fused SiO_2 wedge was used to allow alteration of the reflection plane height. The sample carrier which was also constructed of fused SiO_2 , contained a slotted protrusion cut at a slight angle from the normal. The sample wafer edge rested loosely in this slot.

For intrinsic stress measurements at the oxidation temperature, samples were pre-oxidized at 1100°C to $\sim 4000 \text{ \AA}$ in a manner similar to that reported by EerNisse (6) so as to provide a thick backside oxide, and the front side oxide was removed using an oxide etch procedure previously reported (8). Since under the oxidation conditions used in this study, the rate of oxidation for a thick film on the back side of the wafer is negligible compared to the bare front side, and the film is in a relatively stress-free state when grown at high temperatures, curvature changes during oxidation can be directly attributed to film growth on the front surface. These samples were also cleaned as usual except that the HF dip was omitted.

The furnace was kept at room temperature in flowing N_2 during alignment to minimize oxide growth resulting from back diffusion of O_2 and H_2O from the laboratory ambient into the furnace while the end cap was off. After alignment of the sample, the furnace was ramped to the oxidation temperature and allowed to stabilize, in order to measure the initial curvature point. Then the ambient

was switched to O_2 and the curvature was monitored with time. Since the film thickness could not be measured directly during oxidation with this system, it was estimated using the "optimized X_1 " technique of Massoud (4). Thickness calculations were verified on the in-situ measured samples using ellipsometry after the oxidation was complete. Comparison of these measurements to the estimated thicknesses resulted in an average error of $\sim 10\%$ in thickness which translates to about 10% error in stress.

The thermal expansion stress was obtained in-situ by measuring the wafer curvature during thermal treatment in the presence of a N_2 ambient. With no oxidation taking place, the change in curvature with temperature is directly related to the thermal expansion stress component. While every effort was made to maintain the dryness of the oxidation ambient, the necessary alignment and sample adjustment procedures, as well as the use of a thick backside oxide that was exposed to the laboratory ambient, yielded higher than the usual < 5 ppm H_2O levels during the oxidations and simultaneous stress measurements. That the higher H_2O levels (reported below) affect the stress measurements cannot be excluded in the present study and this is discussed further below.

Experimental Results and Discussion

Stress Measurements.

The in-situ experiments allow for the measurement of intrinsic stress separate from the thermal stress. The curvature

changes in the samples which occur during oxidation are monitored at the oxidation temperature where $\Delta T = 0$ and hence $\sigma_{th} = 0$, as seen in the equation for σ_{th} :

$$\sigma_{th} = (E/(1-\nu)) \Delta\alpha \Delta T \quad (1)$$

where $E/(1-\nu)$ is the composite elastic constant for the film (18) and $\Delta\alpha$ the difference in the coefficients of thermal expansion (CTE) between the film (18) and substrate (19). The thermal stress develops as the sample cools down from the oxidation temperature, ΔT , resulting in compression in the oxide since the CTE for Si is greater than SiO_2 . When total stress is measured at room temperature, the intrinsic stress is obtained by subtracting the thermal stress from the total film stress using the relationship:

$$\sigma_f = \sigma_i + \sigma_{th} \quad (2)$$

where σ_f is the total film stress and σ_{th} is calculated. The value for σ_f is obtained using a revised form of Stoney's original equation (20):

$$\sigma_f = EL_s^2/6(1-\nu)L_fR \quad (3)$$

where $E/(1-\nu)$ is the composite elastic constant for Si (21), L_s and L_f the substrate and film thickness, respectively, and R the radius of curvature. Note that this equation is similar to the general Hooke's law formula:

$$\sigma = E \epsilon \quad (4)$$

where Young's modulus E is replaced by the composite elastic constant $E/(1-\nu)$, and the strain ϵ is represented by L_s^2/L_fR .

Figure 2 shows a comparison of in-situ measurements made during

oxidation in the present study to those obtained sample by sample, i.e. ex-situ, at room temperature (22). The in-situ data is the average of three runs with an average error of $\sim 0.6 \times 10^9$ dynes/cm². With about the same error for the previous data, the in-situ and ex-situ experiments yield the same compressive σ , results. Note that all the data show a greater change in intrinsic stress with thickness in the early stages of oxidation.

The systematic difference in the magnitude of these curves can possibly be attributed to the fact that the in-situ oxidations contained about 15 ppm H₂O, while the ex-situ were done in a conventional double walled furnace having less than 5 ppm H₂O. H₂O is known to cause relaxation effects (11,23). In addition the thick backside SiO₂ film may contain adsorbed H₂O which is released during oxidation and may effect the total curvature. Also, there may be a question as to whether the thick backside SiO₂ film changes at all during the measurements under oxidation conditions.

Figure 3 shows the measured thermal stress as a function of oxidation temperature, where the slope yields the product $E/(1-\nu)\Delta\alpha$ as shown earlier. A least squares fit to the data in Figure 3 resulted in a slope whose value was less than 10% different from the literature values of E and ν (18,19) used to calculate $E/(1-\nu)$. This result is favorable when one considers that the literature values vary by at least this amount. Slight curvature is seen in the data and is possibly the result of the presence of ~ 25 ppm of H₂O inside the furnace during the experiment, which

may result in a small amount of oxide growth at the higher temperatures. This growth will effectively reduce the curvature change. It should be noted that when the larger ΔT values are deleted from this data set to account for possible oxidation, a slope $\sim 15\%$ higher than the original determination is obtained, and the value for $E/(1-\nu)\Delta\alpha$ is $\sim 5\%$ different from the literature values we use (18,19).

Oxidation Kinetics and Viscous Relaxation Effects

First we consider the shape of the intrinsic stress profile as shown in Fig. 2. It is observed that σ_i is larger nearer the Si-SiO₂ interface where SiO₂ is produced via the interface reaction between Si and oxidant. The origin of σ_i has been attributed to the partial confinement of the molar volume change accompanying the transformation (5,7,9). Based on the fact that the maximum σ_i found from extrapolation to zero SiO₂ thickness is substantially less than the theoretical value of more than 10^{11} dynes/cm² (7), an initially fast stress relaxation was suggested for the SiO₂ as it is formed which is followed by a much slower relaxation that is characteristic of the bulk SiO₂ viscosity (22). Several workers (22,23,26) have suggested the existence of a time dependent viscosity where as the oxide grows the viscosity increases from an initial low value for the as forming oxide which is not yet relaxed into the high viscosity form characteristic of the nearly relaxed network structure. Further relaxation occurs for the already formed SiO₂ as this oxide continuously exposed to

the oxidation temperature and pushed out from the interface by newly forming SiO_2 , hence yielding the profile in Fig. 2. The time dependent viscosity was used to explain the production of Si interstitials (26) and stress relaxation phenomena (22,23) which occur as the oxidation or annealing times increase. Corroboration for the stress profile in Fig. 2 was reported (28,29) from infrared spectroscopy, IR, measurements of SiO_2 films where the Si--O--Si bond angle and distribution of angles was obtained. Essentially, it was reported that near the Si- SiO_2 interface, the angle between adjacent tetrahedra became gradually smaller indicating a greater packing of SiO_2 tetrahedra near the Si- SiO_2 interface and with about the same thickness scale as in Fig. 2 for the 800°C oxidation.

Second, from Fig. 2 we consider the extent of the higher stress regime. It is observed both in the present in-situ measurements and previous ex-situ measurements (22), that the extent of the higher σ_i regime is several hundred Å. This is similar to the extent of the initially rapid oxidation regime, L_i , which is observed for the thermal oxidation of Si and which was found not to conform to the kinetics predicted from the linear parabolic model for Si oxidation (1-4). L_i values ranging from 40 to 230 Å have been reported from several authors (1,3,24,25). The qualitative conformity of the rapid oxidation regime with the high stress regime supports the recently proposed stress enhanced oxidation model (10,12) that was proposed as an attempt to explain the effects of σ_i on the interface reaction during thermal

oxidation. This model assumes a proportionality between the linear oxidation rate constant, k_1 , as obtained from the linear parabolic model for oxidation, and stress divided by viscosity as:

$$k_1 \propto \sigma_1 / \eta \quad (5)$$

where η is the oxide viscosity. This model is derived from the notion that the relaxation of the forming SiO_2 in the direction normal to the Si surface, the free direction, which is given by the ratio σ_1 / η in the Maxwell model for a solid, also influences the oxidation rate at the interface. This form is arrived at because the stress relaxation process parallels the growth of oxide in the normal direction to the Si surface and relaxation away from the interface facilitates the formation of new oxide layers. The necessary volume for the new layers of oxide is created by the flow of the already formed SiO_2 away from the interface. The higher the stress and the lower the SiO_2 viscosity, the faster is the flow of formed oxide from the interfacial region and hence the more volume is available to the newly formed oxide. The above cited IR studies (28,29) also show that the bond angle profiles match the stress profiles at all temperatures studied, yielding sharper profiles for higher oxidation temperatures where relaxation takes place more readily. Thus the extent and the evolution with temperature of the stress profiles are corroborated by and consistent with several recent studies.

Summary and Conclusions

The in-situ stress measurements performed in the present study confirm and extend the previous stress measurements on SiO_2 films on Si (8,11,22) as follows:

1. The existence and magnitude of an intrinsic compressive stress in SiO_2 formed via thermal oxidation of Si is confirmed.
2. The magnitude of the thermal expansion stress is confirmed as are the literature values for the thermal expansion coefficients used for Si and SiO_2 , as well as Young's modulus for Si.
3. The profiles for σ , versus oxide thickness are confirmed in both magnitude and spatial extent.
4. The extent of the high stress region has been confirmed in independent SiO_2 film structural studies and is consistent with a previously proposed stress relaxation related oxidation model.

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Figure Captions

- Figure 1. Schematic diagram of laser reflection technique modified to measure film stress at the oxidation temperature (not to scale).
- Figure 2. Comparison of in-situ and room temperature film stress measurements as a function of oxide thickness.
- Figure 3. Thermal stress vs. change in temperature, where the slope yields the product $E/(1-\nu)\Delta\alpha$.

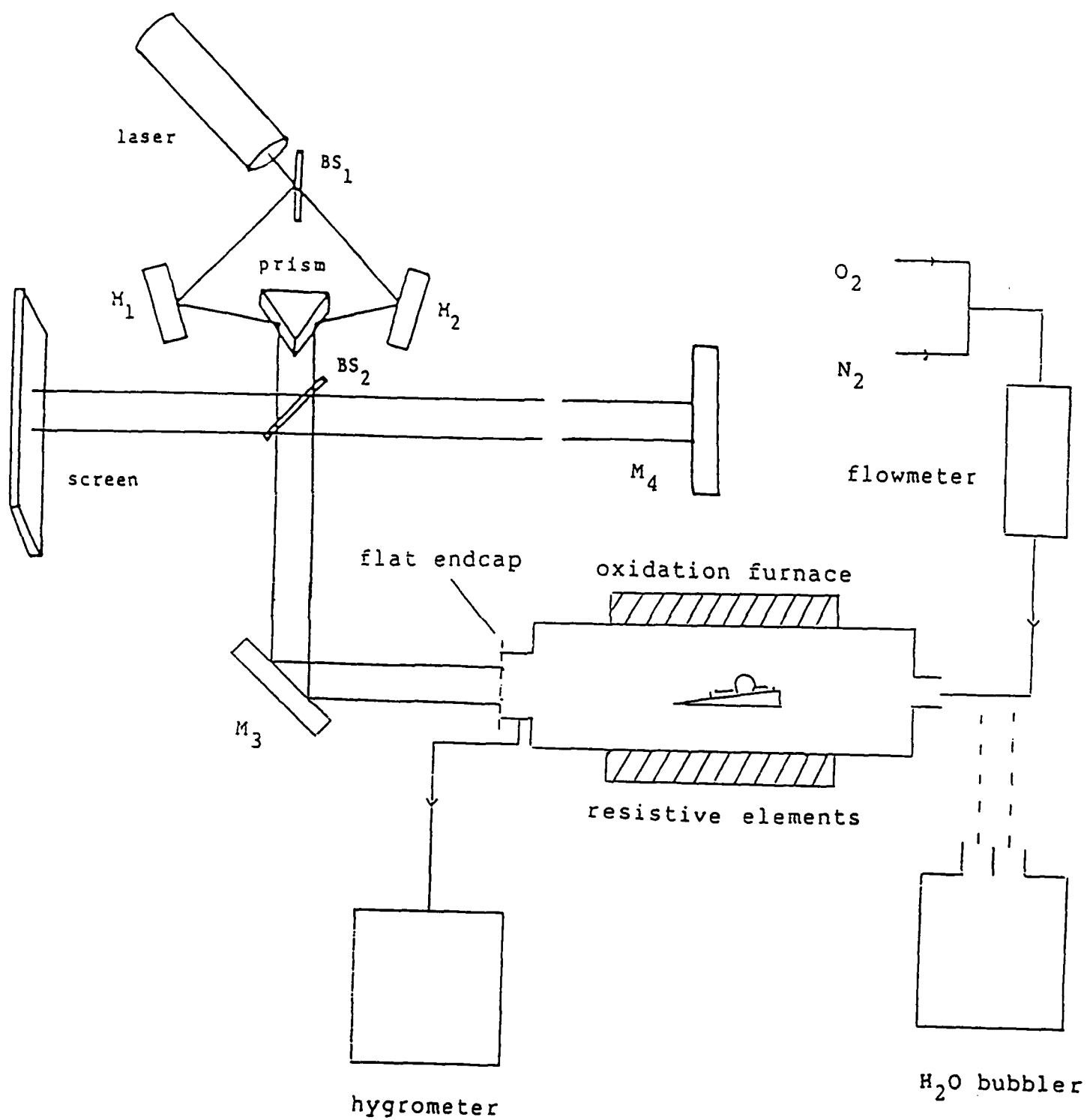


Fig 1

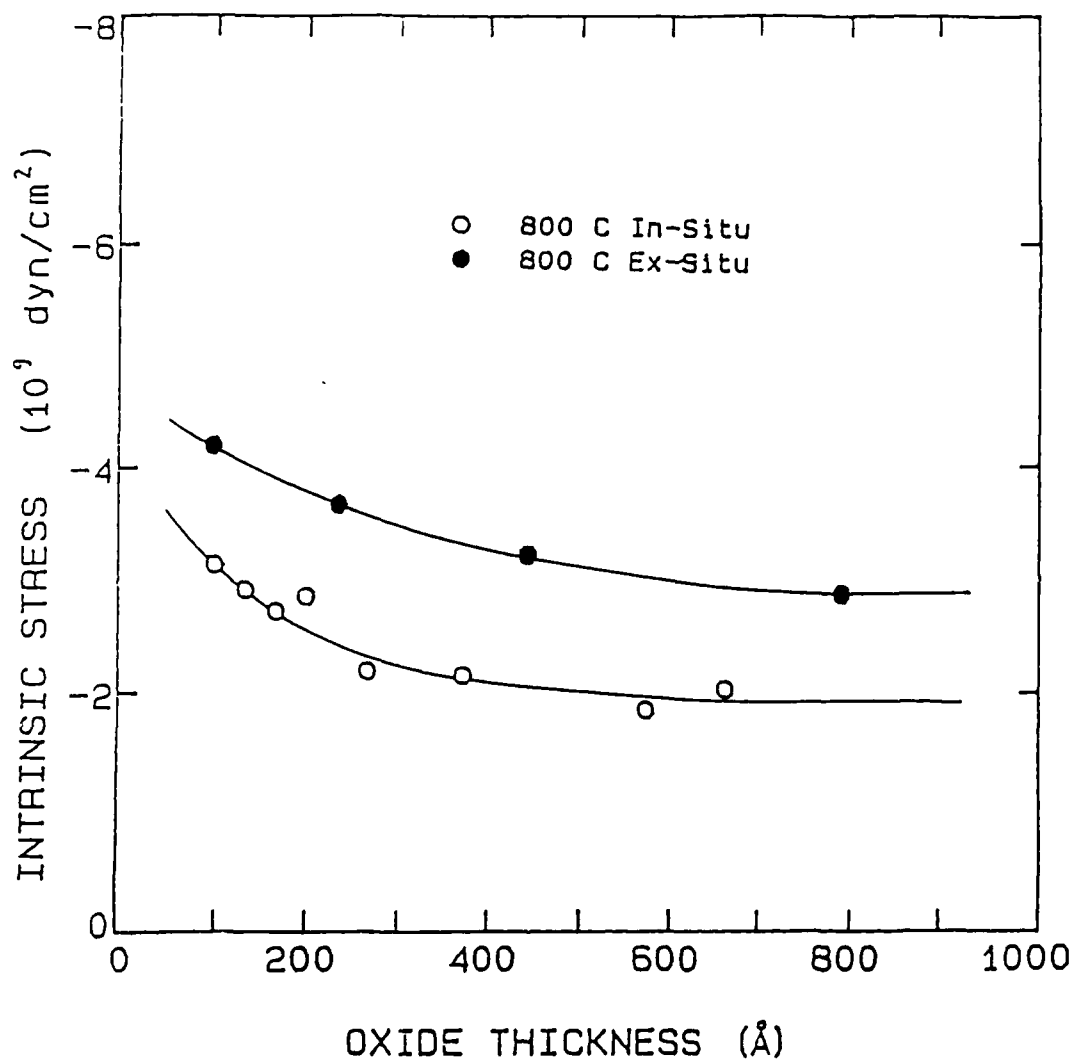


Fig 2

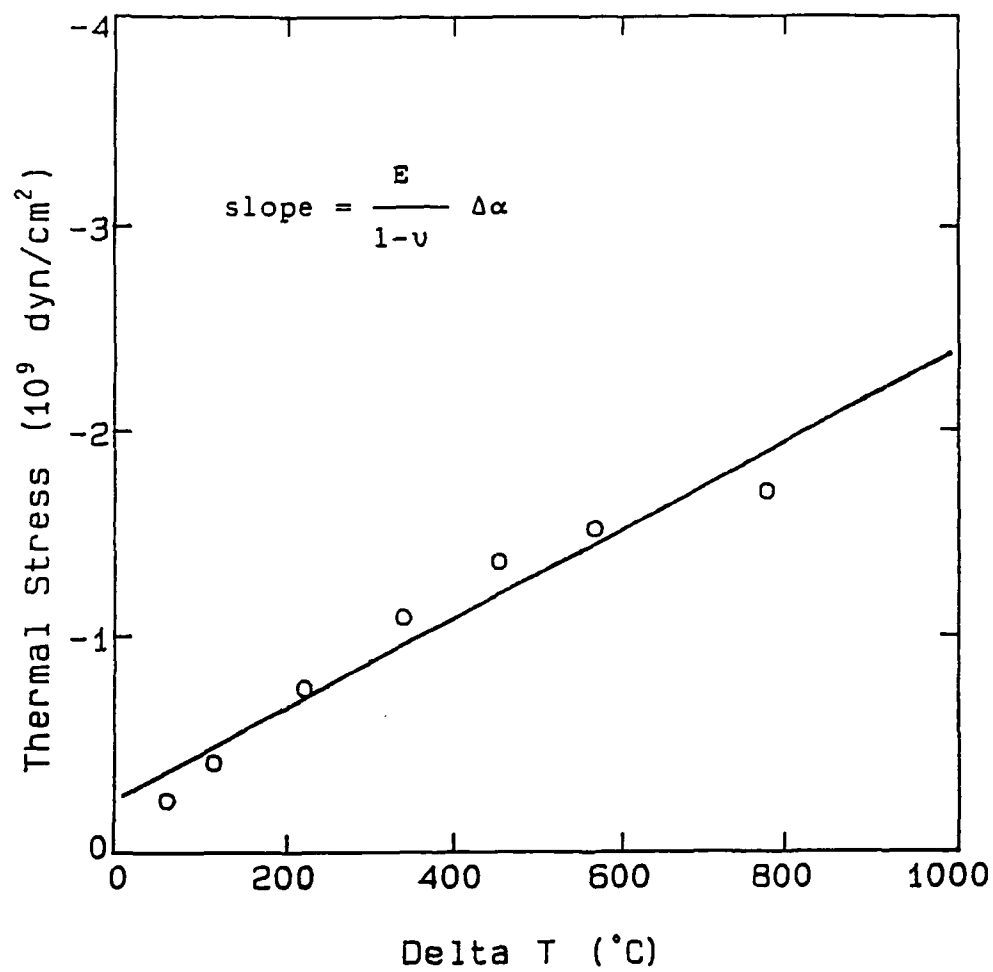


Fig 3