Mechanical Stress in SiO₂ Films Obtained by Remote Plasma-Enhanced Chemical Vapor Deposition

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ABSTRACT

Using a single laser beam reflection technique, the authors have examined mechanical stress in thin SiO₂ films obtained by a remote plasma-enhanced chemical vapor deposition technique. The films were deposited in the 200-600°C temperature range, at a total pressure of 8 mTorr, at 30 or 300 W rf power, using a remote oxygen-plasma silane reaction. All investigated films were found to be in compressive stress at room temperature. Total stress ranged from 1.3 to 2.3×10^9 dynes/cm² (compressive), and the calculated intrinsic stress component ranged from 0.7 to 1.5×10^9 dynes/cm² (compressive). The total compressive stress value was found to be an increasing function of the deposition temperature, due to the increase in the value of the thermal stress component. Total and intrinsic stresses were found to be also dependent on film thickness, thinner films exhibiting higher stress. SiO₂ films deposited using higher rf power (300 W) were found to exhibit a ~20% greater compressive stress than films deposited at the lower power (30 W) level. Post-deposition heat-treatments of the SiO₂ films were conducted to examine stress relief. Both "high" and "low power" oxides showed a partial stress relief after low temperature (300-400°C) inert gas annealing, for anneal times of the order of 100 h. It was found that the stress in "low power" oxides increased to the pre-anneal value when the samples were subsequently re-exposed to a room temperature ambient atmosphere at 35% relative humidity. On the other hand, "high power" oxides did not show any instability when re-exposed to the air. The instability in "low power" oxides was not observed if the films were first annealed at 1000°C for 15 min in oxygen.

In both silicon and compound semiconductor microelectronic technologies, significant effort has been expended in developing low temperature deposition processes for highquality gate oxide films. Among these, it was reported that a remote plasma-enhanced chemical vapor deposition (RPECVD) technique could be used successfully to obtain silicon oxide films with high breakdown fields, low inter-face state densities, and low fixed oxide charge densities.¹⁻³ Little is known, however, about the mechanical properties of these RPECVD SiO₂ films; in particular, about built-in stresses, and how they relate to film parameters, such as thickness, as well as to film processing characteristics. This information is important, since excessive stress in a gate oxide could possibly contribute to the generation of electrical defects in the oxide and/or at the oxide-substrate interface, as well as influence mechanical integrity of both the film and the underlying substrate. Excessive stress in SiO₂ can cause it to crack and/or delaminate, forming voids. Such stress can also impact reliability of overlying metal interconnections if the SiO₂ films are used as interlevel dielectrics.4,5

This paper presents results of an investigation of mechanical stress in SiO_2 films obtained by the RPECVD technique. The stress was studied for films of different thicknesses as a function of process parameters, such as deposition temperature and rf power employed for the generation of the plasma. The influence of post-deposition heat-treatments of varying duration and temperature in inert and oxidizing gas ambient atmospheres on the values of total and intrinsic stresses, and the stability of observed changes was also examined.

Experimental Procedures

The substrates used in this study were double-side polished, 10 mil thick, 4 in. diam, (100) orientation, p-type silicon wafers with resistivities typically in the range 1.5-2.5 Ω -cm. Prior to the deposition, the wafers were cleaned using the standard RCA technique.⁶ The SiO₂ films were deposited at temperatures in the range 200-600°C, at a

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pressure of ~8 mTorr, using the reaction of silane with a remote oxygen rf generated plasma (13.56 MHz).¹ The oxygen to silane ratio was 20 to 1, and the rf power used was either 30 W ("low power"), or 300 W ("high power"). Deposition rates were of the order of 10 Å/min for both power levels. The deposition rate decreases with an increase in the deposition temperature; for example, at 600°C the rate was 2 Å/min. The RPECVD reactor, the details of the deposition procedure, as well as chemical, structural, and electrical properties of RPECVD SiO₂ films are described elsewhere.^{1,2,7,8}

After deposition, any oxide film deposited on the back side of a wafer (the side with a scribed mark) was stripped using a 10:1 buffered HF solution. During the process, the front side of the wafer was protected from the etchant by a layer of photoresist, which subsequently was itself removed in acetone and isopropyl alcohol baths. Oxide thickness and, in some cases, index of refraction were then measured by ellipsometry at a wavelength of 6328 Å.

Oxide film stress was determined through measurements of wafer curvature, using a single laser beam reflection technique. The system and the details of the measurement procedure are described in Ref. 9. The radius of curvature of each of the silicon wafers was measured prior to the deposition of the SiO₂ films, and following such deposition. This allows for the determination of the radius of curvature, *R*, induced by the total stress in the film. Knowing *R*, one can calculate the value of the total stress in the film, σ_t , using the modified Stoney's equation¹⁰

$$\sigma_{\rm f} = \frac{E_{\rm s}}{6(1-v_{\rm s})} \times \frac{t_{\rm s}^2}{t_{\rm f}} \times \frac{1}{R}$$
[1]

where E_s and v_s are the Young's modulus and Poisson's ratio of the substrate, respectively; t_f is the film thickness, and t_s is the substrate thickness. The constant $E_s/(1 - v_s)$ for (100) Si was taken equal to 1.805×10^{12} dynes/cm².¹¹

The total stress determined through curvature measurements is, in the case of interest, assumed to be comprised of two components: an intrinsic stress, σ_i , and a thermal stress, σ_t , as shown in Eq. 2

J. Electrochem. Soc., Vol. 140, No. 2, February 1993 © The Electrochemical Society, Inc.

$$\sigma_{\rm f} = \sigma_{\rm i} + \sigma_{\rm t} \qquad [2]$$

The thermal stress component results from the difference between the thermal expansion coefficients of the film and the substrate, and the cooling of wafers from the deposition temperature to room temperature at which the stress measurements are taken. The thermal stress can be calculated, using the equation

$$\sigma_{\rm t} = \frac{E_{\rm f}}{1 - v_{\rm f}} \times (\alpha_{\rm s} - \alpha_{\rm f}) \times \Delta T$$
[3]

where E_{f} and γ_{i} are the Young's modulus and the Poisson's ratio of the film, α_s and α_f are the thermal coefficients of expansion of the substrate and film, respectively, averaged over the temperature range ΔT , where ΔT represents the difference between the temperature of the stress measurement and the film deposition temperature.¹⁰ In calculations in this paper, values of the $E_t/(1 - v_t)$ and α_t parameters were assumed equal to those of fused SiO₂, *i.e.*, $8.5 \times$ 10^{11} dyne/cm² and 0.55×10^{-6} °C⁻¹, respectively. This assumption seems valid in light of experimental work of Sunami et al. who determined the values for CVD SiO₂ films on the basis of stress vs. temperature measurements, and found α_i equal to $0.55 \times 10^{-6} \text{ °C}^{-1}$, and $E_i/(1 - v_i)$ in the range 7.5×10^{11} - 10.0×10^{11} dyne/cm². ¹² The values for α_s (for silicon) were taken from Ref. 13. Using Eq. 2 and 3, the intrinsic oxide stress can be calculated.

Post-deposition heat-treatments were performed at 300 or 400°C in argon or nitrogen, or at 1000°C in oxygen. The wafer curvature was remeasured following each of the heat-treatments. After all processing was completed, the oxide film was stripped chemically from the substrate, and the bare wafer curvature was measured again. This last step was performed to check whether plastic deformation of the silicon substrate occurred during any of the processing steps.^{9.14,15}

Results and Discussion

General observations.—All the SiO₂ films were found to be in a state of compression at room temperature. The magnitude of stress was found to be in the range $1.3-2.3 \times 10^9$ dynes/cm², depending on film thickness and the deposition conditions, in general agreement with the values obtained for SiO₂ deposited by plasma-enhanced CVD.^{8,16,17} The intrinsic stress, calculated according to Eq. 2 and 3, was in the range $0.7-1.5 \times 10^9$ dynes/cm² (compressive). The intrinsic stress values are smaller than those of thermal oxides and the oxides grown by oxidation of silicon in an oxygen plasma. 9,14,15,18,19 The intrinsic stress for oxides grown at 1000°C can be as high as 3×10^9 dyne/cm². ^{9,15,18,19} The SiO₂ grown by oxidation of silicon in an oxygen plasma at 350°C was reported to exhibit an intrinsic stress in the range $2-3 \times 10^{9}$ dyne/cm². ¹⁴ Unlike remote plasma CVD SiO₂ films and conventional PECVD oxides, both of which exhibit compressive stress, non-plasma LP and AP CVD SiO_2 films generally exhibit intrinsic tensile stress, in the range $2-5 \times 10^9$ dyne/cm². ²⁰⁻²³

Oxide stress vs. oxide film thickness.-Figure 1 shows the value of stress in thin SiO₂ films deposited at 300°C at low (30 W) rf power, plotted as a function of the film thickness. The stress increases as the film thickness decreases. This could be a result of stress relief during the deposition. If such relief occurs, thicker SiO₂ samples would exhibit a lower value of stress, as compared with the thin ones.¹⁵ Another possible explanation is that the value of stress is larger at the substrate-SiO₂ interface than in the bulk of the film, perhaps due to interfacial oxidation of the silicon substrate during the growth of the RPECVD film from the vapor phase.⁷ Whether the stress relief explanation is valid could be deduced via inert gas annealing studies at the deposition temperature, which will be described later.

Stress vs. deposition parameters.-Figure 2 presents stress as a function of deposition temperature for SiO₂ films deposited at low rf power. Film thicknesses were in the range of 400-800 Å. Both the total stress and the intrinsic stresses are shown. Total stress is seen to increase with the

Fig. 1. The dependence of total stress on SiO₂ thickness for films deposited at 300°C with 30 W rf power.

temperature of deposition. This appears to be due to the increase in the thermal component of total stress (proportional to the difference between the deposition temperature and the measurement temperature), as evidenced by the constant value of the intrinsic stress for all the deposition temperatures studied, Fig. 2.

The total stress also appears to be a function of the rf power used for the plasma generation, at least in the investigated range of film thicknesses. In Table I, the values of total stress for films deposited at 300°C using the 30 W power level are compared with the values for films deposited with 300 W power. It is seen that the 30 W samples exhibit a total stress of about 1.5×10^9 dyne/cm² (compressive), rising to 1.8×10^9 dyne/cm² (compressive) at 300 W, an increase of some 20%. The values of the index of refraction and of the etch rates in the P-etchant (HF (49%):HNO3 (70%):H₂O in the volume ratio 15:10:300) are also included. The index of refraction is greater in the "high power" oxides, and the etch rate in the P-etchant is smaller, which is believed to indicate a greater density of the "high power" oxides, relative to films deposited at 30 W rf power.

Influence of post-deposition heat-treatments on the value of stress.—In order to check whether any stress relief occurs at the temperature of deposition, post-deposition heat-treatments of the "low power" SiO2 films deposited at 300°C were conducted. The post-deposition heat-treatment was conducted in argon atmosphere. In Fig. 3, the inverse of the radius of curvature, which is proportional to the value of stress, is plotted as a function of duration of the heat-treatment, and, afterwards, as a function of the duration of storage in a class 1 clean room environment at 22°C and 35% relative humidity. It can be seen in Fig. 3 (from 0 to 148 h) that the stress decreases as the annealing time increases. The value of total stress for the 148 h annealing.

RPECVD SIO2

۳w

RF Power=30

3.0

2.5

2.0

1.5

1.0

(COMPRESSIVE)

n

total stress

intrinsic stress

Ŧ



Ŧ

Ŧ



Table I. Comparison of properties of SiO₂ films deposited at 300°C at 30 W rf power level with those deposited at 300°C at 300 W rf power level.

RF power [W]	Film thickness [Å]	Total compr. stress [10 ⁹ dyne/cm ²]	Refractive index	P-etch rate [Å/s]
30	820	1.46 ± 0.10	1.458	33
30	790	1.59 ± 0.10	1.458	33
300	1010	1.83 ± 0.10	1.467	9
300	1020	1.75 ± 0.10	1.466	9

increases. The value of total stress for the 148 h annealing time is equal to $\sim 66\%$ of the value before the annealing.

Considering these results, in the light of the observed thickness dependence of stress, we note from Fig. 1, that, referenced to the stress in a 220 Å oxide, the change in total stress for a 510 Å oxide is approximately 20%. This reduction in the average total stress occurs in a growth time difference of about 1 h. Examination of Fig. 3 shows that for a 510 Å film, reduction of stress is very rapid initially and tends then to asymptote. Thus, growth time differences can probably explain stress reduction with increasing thickness. However, it is possible that the growth of an interfacial oxide layer contributes to the effect. It has been shown that at the temperature used here for deposition, silicon at a floating potential in a plasma can be oxidized "cathodically." ^{14,24,25} It appears possible that such an effect could take place, at least in the early stages of remote plasma CVD.⁷

Figure 3 shows also the behavior of stress following annealing when the samples were re-exposed to the clean room atmosphere for varying periods of time up to 478 h (cumulative). The stress increases with the storage time, and after about 9 days reaches a value equal to that prior to the annealing. As in the annealing process, the initial change is quite rapid tending to asymptote. The change in the value of stress in samples exposed to air has been observed previously for conventional LPCVD and conventional plasma CVD SiO₂ films.^{26,27} The behavior has been attributed to the absorption of water vapor from the air. By analogy, it is possible that stress relief at 300°C at least partially results from the desorption of water from the sample in a dry inert gas atmosphere.

Figure 4 shows the annealing and subsequent storage behavior of stress in an SiO₂ film which was deposited using the higher (300 W) rf power. The stress decreases after annealing, as for SiO₂ deposited at the lower power level (see Fig. 3), but stays constant when the samples are exposed to the air after the annealing. The stress stability of the "high power" oxides during storage in air seems consistent with the refractive index and etch rate data, which



Fig. 4. Effect of 400°C inert gas annealing, and of subsequent re-exposure to a clean room atmosphere at 35% relative humidity, on the value of stress in an SiO₂ sample deposited at 300°C with 300 W rf power. The value of total stress is directly proportional to the inverse of the radius of curvature.

indicate that oxide films deposited at 300 W rf power are denser than "low power" oxides, and therefore likely to be less permeable to water.

The "low power" oxides were also subjected to a postdeposition heat-treatment at 1000°C in oxygen. This annealing procedure is known to densify LPCVD oxides.^{17,28} Figure 5 shows the effect of this 15 min annealing sequence on the stress value of the "low power" oxide. It is seen that the oxygen annealing results in partial relief of stress, as before. Figure 5 also shows the effect of subsequent exposure to air of this 1000°C annealed oxide. It is seen that the previously observed instability disappears.

Conclusions

SiO₂ films prepared by a remote plasma enhanced chemical vapor deposition (RPECVD) technique with the following process parameters: total pressure 8 mTorr, deposition temperature 200-600°C, and rf power 30 and 300 W, were found to be under compressive stress at room temperature. The stress ranged from $1.3-2.3 \times 10^9$ dynes/cm², depending on the film thickness, temperature of deposition, and rf power. The intrinsic stress calculated by the subtraction of the thermal stress component from the total stress value was found to be independent of the temperature of deposition, but was found to be a function of the film thickness and of the rf power. As the film thickness increases, the stress decreases. The most likely explanation of this effect, particularly in light of the annealing experiments reported in this study, is that a stress relief occurs during the deposition and, because of that, thicker samples which stay at the deposition temperature longer, exhibit a lower value of



Fig. 3. Effect of 300° C inert gas annealing, and of subsequent re-exposure to a clean room atmosphere at 35% relative humidity, on the value of stress in an SiO₂ sample deposited at 300°C with 30 W rf power. The value of total stress is directly proportional to the inverse of the radius of curvature.



Fig. 5. Effect of 1000° C oxygen annealing, and of subsequent re-exposure to a clean room atmosphere at 35% relative humidity, on the value of stress in an SiO₂ sample deposited at 300°C with 30 W rf power. The value of total stress is directly proportional to the inverse of the radius of curvature.

stress. The stress was found to depend also on the rf power level used in the SiO₂ film deposition. The films obtained using the 300 W power level were found to exhibit about 20% greater values of stress, compared with "30 W" oxides. These higher values of stress are accompanied by a greater refractive index, and a smaller P-etch rate, most likely due to a denser structure of the "high power" SiO₂ films, as compared with the ones prepared at 30 W rf power.

Post-deposition heat-treatments, for both "high power" and "low power" oxides, at temperatures approximating the temperature of deposition (300-400°C), were found to cause a partial relief of the stress. Following the heat-treatment, "high power" and "low power" oxides exhibited different behavior when exposed to the air. "Low power" oxides showed the stress increasing with the exposure duration, while "high power" oxides did not show such instability. The increase of stress is believed to be due to the absorption of water vapor from the ambient atmosphere. The stress stability of "high power" oxides studied is consistent with their apparently denser structure, relative to "low power" oxides, as indicated by a higher refractive index and lower P-etch rates. The stress instability in "low power" oxides, when exposed to the air, can be removed by a brief high temperature annealing. For example, the SiO_2 annealed at 1000°C for 15 min in oxygen did not show any instability of the stress value upon subsequent exposure to air, due to, it is believed, film densification during such annealing.

Acknowledgments

Support for this work was provided by the Office of Naval Research in conjunction with the Innovative Science and Technology Office of the Strategic Defense Initiative, by the North Carolina Sematech Center of Excellence, and by the Microelectronics Center of North Carolina (MCNC).

Manuscript submitted April 20, 1992; revised manuscript received Sept. 21, 1992.

MCNC assisted in meeting the publication costs of this article.

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Silicon Etch Using Vapor Phase HF/H₂O and O₃

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ABSTRACT

Gas phase etching of single- and polycrystalline silicon using a mixture of HF/H₂O and O₃ has been investigated. The process proceeds at room temperature without requiring additional excitation sources. The amount of silicon etched depended on the surface doping polarity. The amount of p-type silicon etched was lower than that for n-type silicon, but higher than that for silicon dioxide. The relative roughness of the etched surface depends both on the nature of the surface dopant and on the amount of the silicon etched.

Though there is an abundant array of chemistries for silicon etch, limitations exist for these traditional processes. For example, plasma chemistries may expose the wafers to harmful radiation, and physical sputter etch may cause crystal damage. Consequently, such processes rarely

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are used in cleaning device surfaces prior to the formation of critical components, such as the gate oxide. Wet chemistries typically do not suffer from radiation-induced damage.

One class of such chemistries works by adding oxidizing agents, such as HNO3 1,2 or H2O2, 3 to solutions of HF. Silicon etch is realized by first oxidizing the silicon by the