Thermal Stress in CVD PSG and SiO_2 Films on Silicon Substrates

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ABSTRACT

Stress-temperature relationships of APCVD and LPCVD SiO_2 and PSG films on silicon substrates were measured with the Newton ring method up to 1000°C. Compressive stress in PSG films at room temperature reduces and turns to tension above 100°C. Stress-temperature curves of PSG have a maximum at about 500°C regardless of film compositions and deposition conditions. Heat-treatment of APCVD PSG films at constant temperatures below or above the stress maximum temperature causes an increase or decrease of stress. Stress in APCVD SiO_2 on heating up to 1000°C is tensile while that in LPCVD SiO_2 film changes from compression to tension on heating though both films have the same stress maximum temperature. Stress of the films is attributed to swelling or shrinking caused by water adsorption or desorption up to the stress maximum temperature above which sintering and stress release take place. The stress maximum temperature corresponds to the solidus line in the SiO_2-P_2O_5 binary system.

Silicon dioxide (SiO_2) and phosphosilicate glass (PSG) films prepared with chemical vapor deposition (CVD) are widely used on IC and LSI circuits for protection or passivation of aluminum interconnect lines. One of the serious problems in this application is stress formation in the films. Since the stress causes cracks that reduce the reliability of circuits, several investigations have been carried out, and many factors such as composition of the films, deposition conditions, and humidity in surroundings are known to affect the stress (1-5). Above all, the effect of heat-treatment is important not only for optimization of the circuit fabrication process but also for investigation of the stress propagation mechanism (6). However, most of the former research efforts were based on room temperature measurement which includes stress developed during cooling.

In this work, stress-temperature relationships of SiO_2 and PSG films with various phosphorus concentrations and different preparation methods were investigated by using a convenient apparatus with which a curvature of wafers in a heating furnace can be directly measured up to 1000°C with the Newton ring method (7).

Direct measurement of the thermal stress in SiO_2 films was reported by Sinha *et al.* (8).

Recently, Sintani *et al.* (9) have reported *in situ* measurement of stress-temperature relationships of CVD PSG and SiO_2 films by using x-ray diffraction, and they discussed the results in relation to water adsorption or desorption and high temperature creeping. Their report is consistent with our work basically, but more refined measurements are presented in this paper; and the stress propagation mechanism is qualitatively discussed.

Experimental

SiO_2 and PSG films of 500-1200 nm in thickness were formed on (100) silicon plane wafers at 3 in. diam and 0.45 mm thick with atmospheric CVD (APCVD) and low pressure CVD (LPCVD) at 0.1-0.2 Torr. Deposition temperatures were 380° and 500°C for APCVD and 430°C for LPCVD. Deposition rates of the films are 500 A/min for APCVD and 50 A/min for LPCVD. In both cases, the O_2/SiH_4 ratio was kept constant (12 and 2.5) and PH_3 diluted with N_2 was introduced in the reactor as the phosphorus source. Phosphorus content in the films was determined by x-ray fluorescence analysis. All samples before measurement were stored for 1-3 weeks at room temperature without humidity control.

An apparatus designed for stress measurement is shown schematically in Fig. 1. A sample wafer 22 mm in diameter, which was cut from an initial 3 in. wafer, was placed on an optically flat plate of quartz glass in a vertical electric furnace of about 30 mm internal diameter. Interference fringes of reflected light between the wafer and the quartz glass surface were detected through a half-mirror and a telescope using a sodium lamp as the light source, and the radius of curvature of the wafer was calculated (7). Temperature of the furnace was increased and decreased at the rate of 250°C/hr. Before this experiment, direction and magnitude of curvature of the wafers were measured with a laser flatness tester (Cannon Corporation, LSF-500). Sensitivity of this experiment is limited by (*i*) uncertainty of center position of the samples and (*ii*) anisotropic deformation of the curvature. The error caused by (*i*) could be minimized to less than one-half of the wavelength by careful measurements, but a discrepancy of more than 20% in curvature between two perpendicular directions of wafers took place in some samples. Mean values were chosen in these cases.

The stress was calculated from the following formula reported by Jacodine *et al.* (10)

$$\sigma = \frac{1}{6}\frac{E}{1-\nu}\frac{1}{R}\frac{t_s^2}{t_g}$$

where σ is the stress in the film, E and ν are Young's modulus and Poisson ratio of silicon, respectively, t_g and t_s are thickness of films and wafers, respectively, and R is the radius of curvature.

Results

Stress-temperature relationships.—Figure 2 shows the stress-temperature relationships of APCVD films

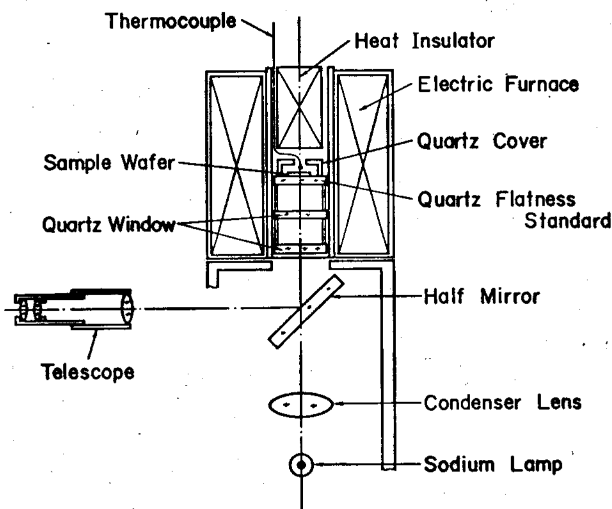

Fig. 1. Schematic view of experimental apparatus

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Key words: stress-temperature relationship, heat-treatment, stress propagation mechanism.

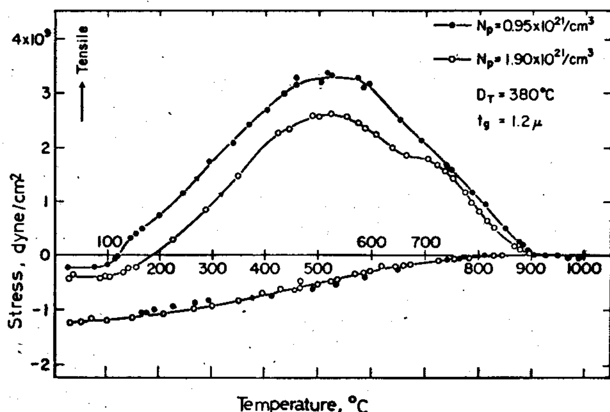

Fig. 2. Stress-temperature relationship of APCVD PSG films deposited at 380°C.

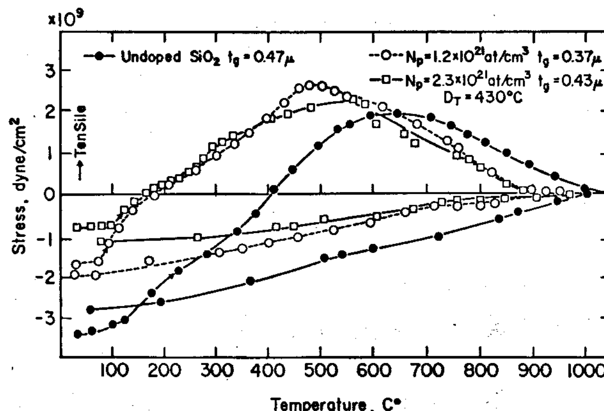

Fig. 4. Stress-temperature relationship of LPCVD SiO_2 and PSG films.

deposited at 380°C. The initial stress before heating is compressive. This may be caused by the long storage time of samples, as is shown below. Above 100°C, the stress decreases and changes to tensile with increasing temperature. The stress reaches a maximum at about 500°C, then decreases, and completely disappears above 900°C. On cooling, compressive stress develops below about 700°C and increases with decreasing temperature. A small hump at about 700°C is observed in some samples though we failed to connect it to any sample preparation process or composition.

Figure 3 also shows the stress-temperature relationship of APCVD PSG and SiO_2 films deposited at 500°C. Similar results can be observed except for SiO_2 film where the initial stress is tensile, and the tensile stress remains until 1000°C. The stress maximum temperature of the SiO_2 film is about 700°C. When phosphorus content is above 2.8×10^{21} atoms/cm^3 ($\simeq$6 mol percent P_2O_5) no significant stress can be observed at any temperature.

Figure 4 shows stress of LPCVD films of various phosphorus concentrations in relation to temperature. In contrast to APCVD films, initial stress of SiO_2 films is compressive although the stress maximum temperature is approximately the same as that of APCVD films. In the case of PSG films, behavior of stress is similar to that of APCVD.

Stress maximum temperature and maximum stress are shown in Fig. 5 in relation to phosphorus concentration in the films. Maximum stress of APCVD decreases with increasing phosphorus concentration, but only a slight decrease of the stress is observed in LPCVD PSG films. On the other hand, the stress maximum temperature of PSG films is constant regardless of deposition method or phosphorus content.

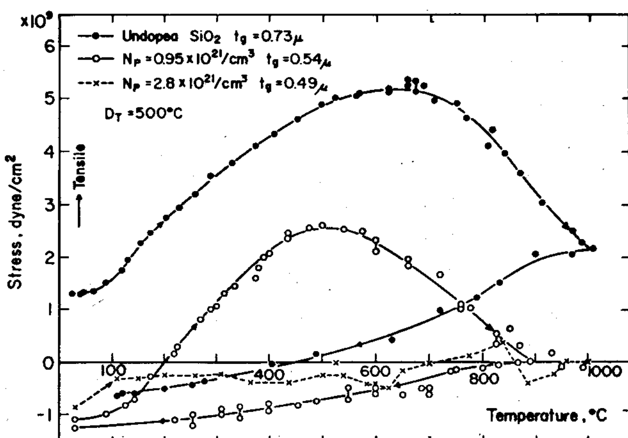

Fig. 3. Stress-temperature relationship of APCVD SiO_2 and PSG films deposited at 500°C.

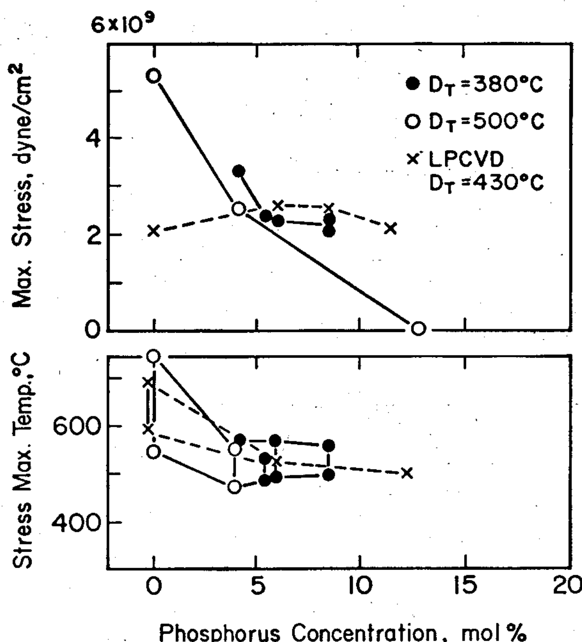

Fig. 5. Maximum stress and stress maximum temperature of APCVD and LPCVD PSG films in relation to phosphorus concentration.

Effect of heat-treatment.—Figures 6 and 7 show stress-temperature relationships of APCVD films under various heating cycles. When the films are kept at constant temperature near, but below or above, the stress maximum temperature, stress increases or decreases with time, respectively. On cooling, stress decreases monotonously. Further decrease in stress is observed after storage at room temperature, if heat-treatment temperature is limited below the stress maximum temperature, though its rate is small. When the sample was reheated, the stress increased nearly parallel to the cooling curve up to the initial heating temperature. Above that temperature, the stress-temperature curves change similar to that shown in Fig. 2 and 3. Similar stress-temperature loops are observed on LPCVD PSG films.

Time dependence of the stress in APCVD PSG films heat-treated at constant temperature is shown in Fig. 8. Stress increases or decreases with time when the heat-treatment temperature is below or above the stress maximum temperature.

Change of stress after deposition.—Figure 9 shows change of stress in APCVD PSG films stored at room temperature in relation to the phosphorus concentrations. Stress in films just after deposition is tensile, but it decreases or turns to compression after one week.

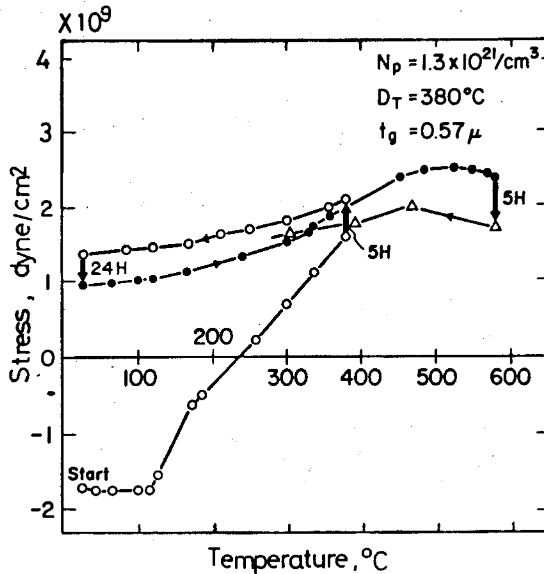

Fig. 6. Stress-temperature relationship of APCVD PSG films under various heat-treatments.

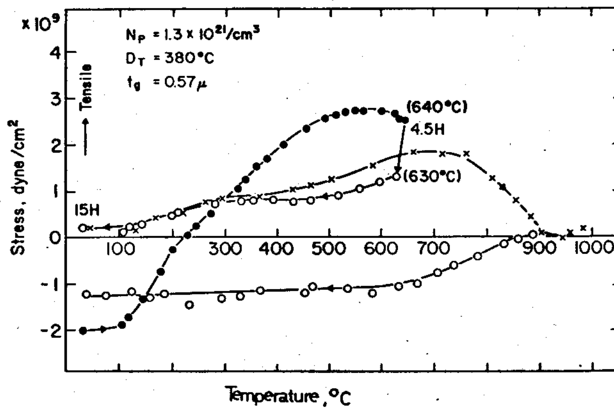

Fig. 7. Stress-temperature relationship of a APCVD PSG film heat-treated above the stress maximum temperature.

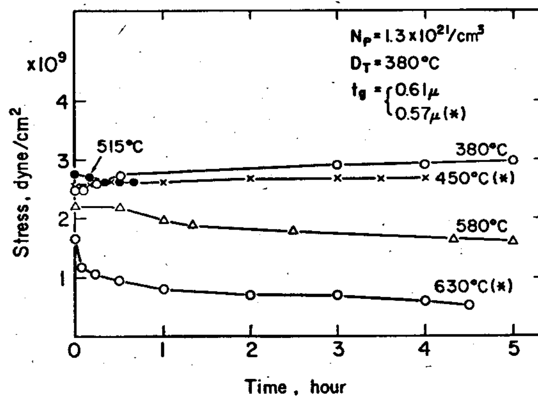

Fig. 8. Stress in APCVD PSG films in relation to heating time at various temperatures.

Similar results have been reported by Sunami (5). These phenomena are explained as the swelling of films with adsorption of water.

Discussion

Pulker (6) reported that the total stress developed in films originates from (*i*) redistribution of incomplete structural order, (*ii*) the chemical and physical incorporating materials, and (*iii*) thermal expansion difference between the films and substrates. The total stress in CVD PSG and SiO_2 films can be explained by

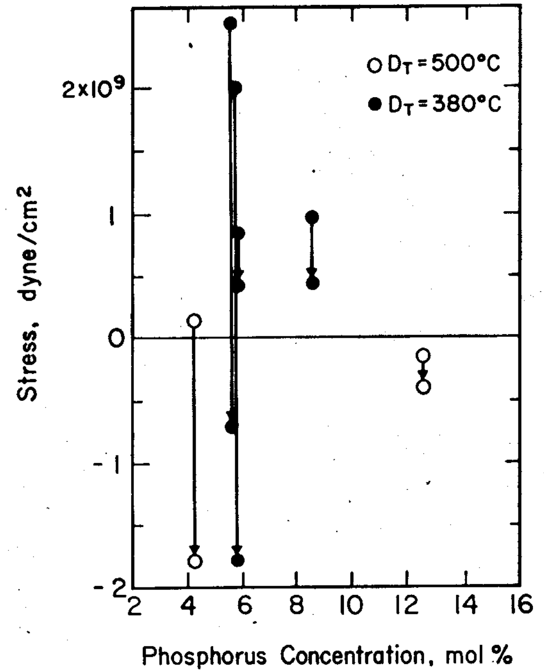

Fig. 9. Change of stress in APCVD PSG films at room temperature after deposition in relation to phosphorus concentration in the films.

using similar mechanisms. Quantitative separation of the above factors, however, is quite difficult in our experiment because they are supposed to be correlated with each other, and many physical constants of the films (ν, E, etc.) are unknown. Therefore the dominant process contributing to the total stress will be qualitatively proposed.

Stress-temperature relationships up to the stress maximum temperature can be explained if we assume that CVD films are porous in nature like silica gel or porous glass, and water molecules are absorbed or desorbed to reach an equilibrium determined with temperature and humidity (11, 12). LPCVD SiO_2 films which absorb much water (9) swell to propagate compressive stress at room temperature, while tensile stress develops on APCVD SiO_2 films in which swelling with water is not sufficient to compensate shrinkage which may be based on the above mechanism (*i*) according to Pulker. In the case of PSG films, behavior of stress is similar to that of LPCVD SiO_2 but sign and magnitude of initial stress depend on their composition and deposition conditions together with the storage time under humidity. Above 100°C, all films shrink with dehydration up to the stress maximum temperature.

Some irreversible dehydration polymerization may proceed in this temperature range because the stress reducing rate of the films heat-treated below the stress maximum temperature is small at room temperature (cf. Fig. 6). But change of the maximum stress could not be detected after annealing the films below the stress maximum temperature. Above the stress maximum temperature, the total stress reduces with sintering and creeping of films (9).

The stress maximum temperature of PSG films is constant, and is consistent with the solidus line in the SiO_2-P_2O_5 phase diagram (13). The phase diagram also shows that the stable phase of PSG films may be a mixture of SiO_2 and low melting phosphosilicates.

Segregation of constituents in some PSG films during deposition is plausible because the high temperature hump shown in Fig. 2 coincides with the stress maximum temperature of SiO_2 films shown in Fig. 3. PSG films completely melt and flow above 900°C, and stresses caused by thermal expansion difference between substrates and films develop below the strain

temperature (about 700°C for PSG films) during cooling. Cooling curves of the stress shown in Fig. 6 and 7 suggest that reduction of stress in annealed films on cooling is also caused mainly by the thermal expansion difference. But change of the stress in these films was larger than that in the remelted films under the same temperature change. This suggests that the mechanical constants (E and ν) or the thermal expansion coefficient of annealed and sintered films are not equal.

Conclusion

Stress of APCVD SiO_2 films on heating is tensile (from room temperature to 1000°C) and has a maximum at about 700°C, while that of LPCVD SiO_2 changes from compression to tension, though its maximum temperature coincides with the former. In the case of PSG, the stress temperature curves resemble that of LPCVD SiO_2, but have a maximum at about 500°C regardless of film compositions and preparation conditions.

Stress of films is attributed to swelling or shrinking caused by water adsorption or desorption up to the stress maximum temperature above which sintering and stress release with creep proceed. The stress maximum temperature from which sintering proceeds corresponds to the solidus line in SiO_2-P_2O_5 binary system. Segregation of constituent in some PSG films between SiO_2 and low melting glass before heat-treatments is plausible.

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