

# Stress in Liquid-Phase Deposited Oxide Films

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## ABSTRACT

To develop a low-stress dielectric thin film, a novel liquid-phase deposition (LPD) technique utilizing silica-saturated hydrofluosilicic ( $\text{H}_2\text{SiF}_6$ ) solution with only  $\text{H}_2\text{O}$  added is proposed. Due to fluorine incorporation, the stress in as-deposited LPD oxide can be as low as 83.3 MPa (tensile). Addition of  $\text{H}_2\text{O}$  greatly affects the stresses in as-deposited LPD oxide: the less  $\text{H}_2\text{O}$  added, the lower the stress will be. The stress variations accompanying thermal cycling have also been clarified. Films deposited with a larger quantity of  $\text{H}_2\text{O}$  added exhibited larger stress variations (hysteresis). After *ex situ* annealing at around 600°C, the total stress decreased to near 0 MPa.

To meet future high-density and high-performance requirements for ultralarge scale integration (ULSI) devices, multilevel interconnection has become more important than ever. For multilevel interconnection, low-temperature formation of fully planarized interlayer dielectric film is a key technology. To realize this technology, a selective deposition method that is independent of the pattern aspect ratio is essential.<sup>1</sup>

In addition to planarization, stress in interlayer dielectric films also has significant effects on the reliability of multilevel interconnections.<sup>2</sup> Excessive stress in dielectrics makes films crack easily and/or delaminate,<sup>3</sup> or induces voids in the interconnections.<sup>4,5</sup> To develop a reliable interlayer dielectric film for multilevel interconnection, investigation into film stress is indispensable.

Recently, a newly developed liquid-phase deposition (LPD) technique has been shown to be capable of selectively depositing silicon oxide films at room temperature.<sup>1,6</sup> Excellent physicochemical and electrical properties of LPD oxide have also been reported.<sup>7,8</sup> In particular, it has been found that fluorine atoms can be incorporated naturally, into the LPD oxide during deposition.<sup>9</sup> Therefore, the LPD method is potentially applicable to the formation of interlayer dielectric films for multilevel interconnection. In a previous study,<sup>9</sup> we reported that the quantity of  $\text{H}_2\text{O}$  added can greatly affect the physicochemical properties of LPD oxide. However, to date, stress in LPD oxide has not been investigated. In this paper, the effects of added  $\text{H}_2\text{O}$  on stresses in LPD oxide are investigated in detail. Variations in stresses in LPD oxide during *in situ* and *ex situ* thermal cycling are also clarified.

## Oxide Stress

Oxide stress ( $\sigma_T$ ) has two components, intrinsic stress ( $\sigma_{in}$ ) and thermal stress ( $\sigma_{th}$ ), *i.e.*

$$\sigma_T = \sigma_{in} + \sigma_{th} \quad [1]$$

The intrinsic stress component results mainly from bonding between Si, O, and OH, and can be either tensile or compressive. The thermal stress component, on the other hand, is attributable to a difference in thermal expansion coefficients between films and substrates that can cause differential contraction during cooling from deposition temperature to ambient temperature, and is given by<sup>10</sup>

$$\sigma_{th} = E_f / (1 - \nu_f) \int_{T_a}^{T_d} (\alpha_f - \alpha_s) dT \quad [2]$$

where  $E_f$  is the Young modulus for the film,  $\nu_f$  is the Poisson ratio of the film,  $\alpha_f$  and  $\alpha_s$  are the thermal expansion coefficients of, respectively, the substrates and the films, and  $T_d$  and  $T_a$  are, respectively, the deposition and stress-measurement temperatures. In the case of  $\text{SiO}_2$  film on Si substrates,  $E_f / (1 - \nu_f)$  is equal to  $8.5 \times 10^{11}$  dyn/cm<sup>2</sup>, and if  $\alpha_f$  and  $\alpha_s$  do not change with temperature, then the above equation can be simplified to

$$\sigma_{th} = \left( \frac{E_f}{1 - \nu_f} \right) \cdot (\alpha_f - \alpha_s) \cdot (T_d - T_a) \quad [3]$$

Since  $\alpha_s$  ( $3.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) is usually larger than  $\alpha_f$  ( $0.55 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) is for  $\text{SiO}_2$  films on Si substrates, and  $T_d$  is usually larger than  $T_a$ , the resulting stress become compressive at room temperature.

## Experimental

**Sample preparation.**—Four inch p-type (100) 15 ~ 25  $\Omega$ -cm silicon wafers were used as substrates in all experiments. The wafers were cleaned using standard processes and the native oxide that formed during cleaning ( $\text{HCl} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ ) was not removed. The initial radius of curvature of each wafer was measured by means of a single-laser reflection technique employing a Tencor FLX-2320 thin-film stress-measurement instrument.

An aqueous solution consisting of 75 g of 99.99% pure silica powder added to 1750 ml of 4 mol/liter hydrosilicofluoric acid ( $\text{H}_2\text{SiF}_6$ ) was prepared and saturated with silicic acid [ $\text{Si}(\text{OH})_4$ ].<sup>9</sup> To supersaturate the solution, deionized water ( $\text{H}_2\text{O}$ ) was later added as described below.

The prepared wafers were immersed in solutions containing 250 ~ 750 ml of added  $\text{H}_2\text{O}$  per 1000 ml of saturated solution to deposit 1700 Å thick LPD oxide films. The deposition temperature of 25°C was carefully controlled by means of water bath and immersion times (shown in the table inset in Fig. 1) were varied according to the amount of  $\text{H}_2\text{O}$  added to control oxide thickness.

In preparation for stress measurements, film deposited on the back sides of wafers was stripped away using a buffered HF solution.

**Stress measurements.**—Stresses in deposited oxides were calculated by determining changes in wafer radii of curvature after deposition according to the following equation<sup>11,12</sup>

$$\sigma = \frac{E_s}{6(1 - \nu_s)} \cdot \left( \frac{t_s^2}{t_f} \right) \cdot \left( \frac{1}{R_2} - \frac{1}{R_1} \right) \quad [4]$$

where  $E_s$  and  $\nu_s$  are, respectively, the Young modulus and Poisson ratio of Si,  $t_f$  and  $t_s$  are the thickness of the LPD oxide and Si substrate, respectively, and  $R_1$  and  $R_2$  are, respectively, the wafer radii of curvature before and after LPD oxide deposition.

To clarify the LPD oxide stress variations during *in situ* thermal cycling, periodic stress measurements were made as wafers with LPD oxide films were heated from 25 to 450°C in an  $\text{N}_2$  atmosphere at a ramped rate of 8.5°C/min, then cooled back down to 25°C at 1.6°C/min. Separate stress measurements were made after reheating the thermally cycled wafers to 450°C in  $\text{N}_2$  ambient for 30 min to check the final equilibrated stresses. And since during actual processing the stresses built up by annealing may exert a significant impact on interconnections,<sup>13</sup> 2200 Å thick LPD oxide films made with 375 and 750 ml of added  $\text{H}_2\text{O}$  per 1000 ml of saturated solution were heat-treated *ex situ* at 400 ~ 1000°C in  $\text{N}_2$  ambient for 30 min, with stress measurements being made immediately after each treatment.

Finally, to determine fluorine concentrations in the top layers of LPD oxides after all annealings, x-ray photo-

electron spectroscopy (XPS) was performed at a single take-off angle using a Perkin-Elmer Model 1600 spectrometer.

### Results and Discussion

**LPD oxide stress.**—Figure 1 shows the dependence of stress on the quantity of added H<sub>2</sub>O for 1700 Å thick LPD oxides. All the stresses were found to be tensile and to possess magnitudes ranging from 80 to 110 MPa. These values are much lower than the 200 ~ 500 MPa of CVD oxides.<sup>14-16</sup> In this figure, we can also see that the stress shows a strong dependence of the quantity of added H<sub>2</sub>O.

Since the deposition and measurement temperatures are nearly the same (room temperature), the total stress in as-deposited LPD oxide must result mainly from intrinsic stress. The intrinsic stress in LPD oxide may be caused by bond strains originating from the dehydration reaction during deposition. When Si-O-Si bonding takes place after dehydration, there must be a large puckering strain.<sup>17</sup> If sufficient energy is not applied to the oxide, bond strains will remain and result in intrinsic stress. Since the dehydration reaction causes shrinkage of the film, the intrinsic stress must be tensile.<sup>18</sup>

LPD oxide deposited with 250 ml of H<sub>2</sub>O added shows a stress of 83.3 MPa, while films deposited with 375 and 500 ml of H<sub>2</sub>O added show stresses near 103.3 MPa. However, the film deposited with 750 ml of H<sub>2</sub>O added only shows a slight increase in comparison with that deposited with 500 ml of H<sub>2</sub>O added, leading to the conclusion that the less H<sub>2</sub>O added, the lower the stress was in the LPD oxide. The lower stress may be due to the effect of fluorine atoms incorporated in the film. We reported in our previous study that the less H<sub>2</sub>O added to the solution, the more fluorine atoms were likely to be incorporated into the LPD oxide.<sup>19</sup> The stress could be reduced by increased fluorine incorporation in the oxide.<sup>20-22</sup> A possible mechanism leading to the stress reduction is the interaction of fluorine atoms with strained Si-O bonds, forming Si-F and nonbridging bonds, which result in local strain relaxations.<sup>23</sup> Thus, the lower stresses in LPD oxides deposited with less H<sub>2</sub>O added can be attributed to an increase in fluorine atoms incorporated in the films.

The discussion above suggests that the stress in LPD oxide should increase linearly with increasing quantities of added H<sub>2</sub>O because fluorine atoms incorporated in the LPD oxide are decreasing linearly with increased quantities of added H<sub>2</sub>O.<sup>19</sup> However, in Fig. 1, we see that there is only a slight increase in stress in samples deposited with 750 ml of H<sub>2</sub>O added. The relatively minor difference in

stress may be due to many more OH-related bonds contained in films prepared with 750 ml of H<sub>2</sub>O added, because tensile stress is reduced when OH-related bonds are present.<sup>24,25</sup> Why more OH-related bonds are contained in films with larger quantities of added H<sub>2</sub>O can be explained as follows: when H<sub>2</sub>O is added to a saturated H<sub>2</sub>SiF<sub>6</sub> solution, the silicic monomer Si(OH)<sub>4</sub> is formed and then absorbed by the substrate surface. Acid-catalytic dehydration occurs between these silicic monomers, followed by Si-O-Si bond formation. The more H<sub>2</sub>O added, the less likely the dehydration reaction is to be completely finished in time, and the larger the number of residual OH bonds remaining in the film. However, since it is difficult to quantify OH-related bonds contained in LPD oxides, we cannot directly prove these inferences at present; work on quantifying OH-related bonds in LPD oxide is still in progress.

**Stress variation during *in situ* thermal cycling.**—Variations in total stress during *in situ* thermal cycling for 1700 Å thick LPD oxides prepared with 75, 500, 375, and 250 ml of H<sub>2</sub>O added are shown in Fig. 2a-d, respectively. It should be noted that the *y*-axis scales in these figures are not the same for all four samples. The samples all show that total stress tends to become more tensile when the annealing temperature is increased to 450°C. During the subsequent cooling cycling, the total stress becomes less tensile with decreasing temperature, but the final value of total stress in thermal annealing is larger than the initial value. That is, the total stress variation shows hysteresis over the course of thermal cycling. As mentioned above, total stress in thin film includes two components: thermal stress and intrinsic stress. During thermal cycling, both thermal stress and intrinsic stress may change with temperature. According to Eq. 3, thermal stress has a linear relationship with temperature, and becomes more tensile as temperature increases, less tensile as temperature decreases. If no intrinsic stress developed in the film during thermal cycling, the variation in total stress should follow the linear variation in thermal stress only, and show no hysteresis. However, the hysteresis shown in Fig. 2 suggests that some intrinsic stress developed in the LPD oxide during thermal cycling.

The development of intrinsic stress in LPD oxide during thermal cycling is due to changes in the oxide structure, especially the escape of OH-related bonds, and formation of additional Si-O-Si bonds. Si-O-Si bond formation can give rise to a large number of bond strains. If the bond strains are not relieved, they will result in intrinsic tensile stress in the film. With increasing temperature, an increase in intrinsic tensile stress can develop in the oxide, and consequently make the total stress more tensile. If a large intrinsic tensile stress is left in the film at the beginning of the subsequent cooling cycle, it will remain constant with decreasing cooling temperature. Thus, the combination of thermal stress and intrinsic stress will make total stress during cooling larger than that during heating, allowing hysteresis to occur.

The hysteresis scale can be calculated from the difference between the initially measured stress and the finally equilibrated stress. The dependence of hysteresis stress in 1700 Å thick LPD oxides on the quantity of added H<sub>2</sub>O was calculated, and is shown in Fig. 3. In this figure, we can clearly see that the more H<sub>2</sub>O added, the greater the hysteresis. That is, in LPD oxide deposited with more H<sub>2</sub>O, a larger intrinsic stress developed during thermal cycling. Since the hysteresis is attributable to residual OH-related bonds, the results shown in Fig. 3 are consistent with the observation that more OH-related bonds are contained in LPD oxides deposited with larger quantities of added H<sub>2</sub>O.

**Stress variation during *ex situ* thermal cycling.**—Total stress ( $\sigma_T$ ) in LPD oxide annealed *ex situ* was also investigated. The dependence of  $\sigma_T$  on annealing temperature is shown in Fig. 4. Samples deposited with 375 and 750 ml of H<sub>2</sub>O added were compared, and it was found that both exhibited similar characteristics. The maximum tensile

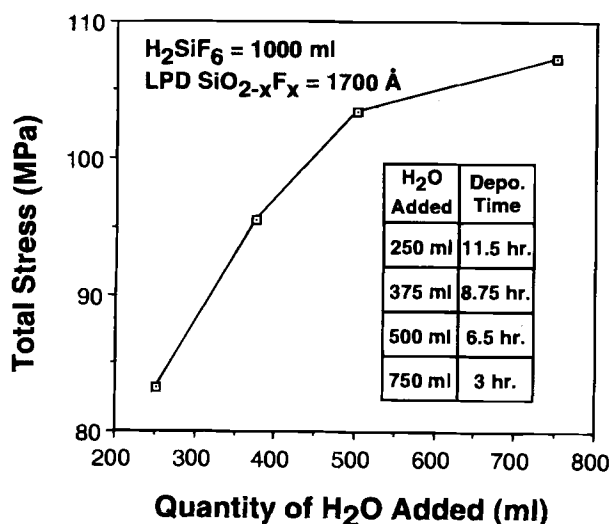


Fig. 1. Dependence of stress on the quantity of H<sub>2</sub>O added for 1700 Å thick LPD oxides. The inset shows the deposition time used to yield the oxide thickness for different quantities of added H<sub>2</sub>O.

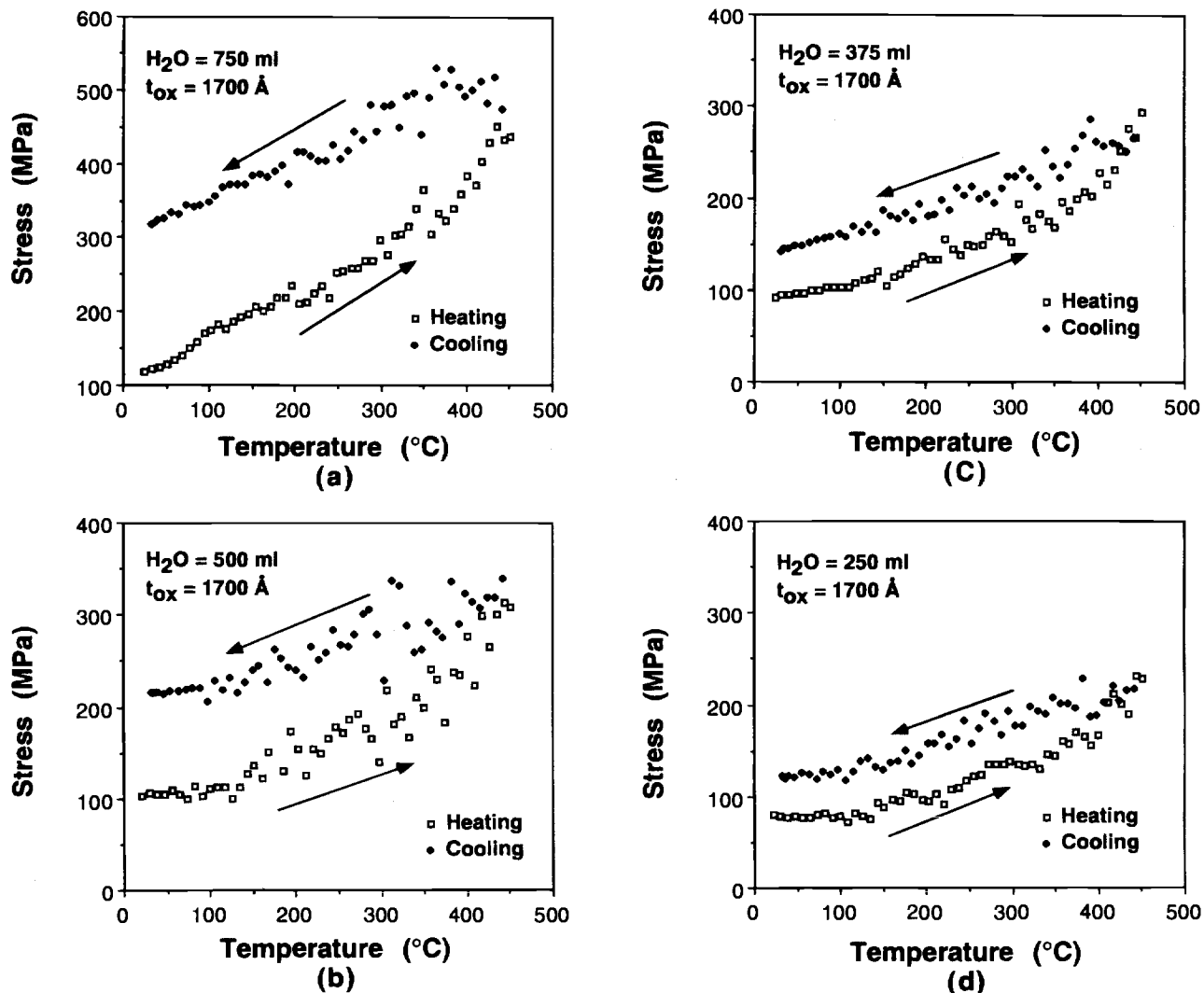


Fig. 2. Variations in total stress during *in situ* thermal cycling (25 ~ 450°C) for 1700 Å thick LPD oxides deposited with (a) 750, (b) 500, (c) 375, and (d) 250 ml of H<sub>2</sub>O added to 1000 ml of saturated H<sub>2</sub>SiF<sub>6</sub> solution.

stress was found in films annealed at 400°C, with  $\sigma_T$  beginning to decrease with increasing temperatures over 400°C. It then decreased to compressive stress after annealing at 600°C. When the film was annealed at 800°C, the  $\sigma_T$  increased again. However, after annealing at 1000°C, the  $\sigma_T$  decreased toward more compressive stress. This clearly indicates that intrinsic stress developed in the LPD oxide film during *ex situ* thermal cycling probably owing to structural changes. To study these structural changes further during thermal cycling, variations in intrinsic stress ( $\sigma_{in}$ ) with temperature were obtained by subtracting the calculated thermal stress ( $\sigma_{th}$ ) from  $\sigma_T$ , as shown in Fig. 5. The characteristics of  $\sigma_{in}$  are similar to those of  $\sigma_T$  except for the difference in scale.

As mentioned above, the OH-related bonds contained in the film escape with annealing at 400°C. Annealing causes the LPD oxide to undergo densification via the formation of additional Si-O-Si bonds, which can give rise to bond strains. If the bond strains are not relieved, intrinsic stress in the film increases. Thus, intrinsic stress increased after annealing at 400°C. Further increasing annealing temperature to 600°C gave structural atoms in the film sufficient energy to move locally. This not only caused bond restructuring, but also relieved the bond strains, and hence, reduced intrinsic tensile stress.<sup>13</sup> There seems to exist a threshold temperature beyond which the intrinsic tensile stress in LPD oxide decreases.

The fact that intrinsic stress becomes increasingly more tensile again at annealing temperatures over 600°C may be accounted for by the removal of fluorine atoms from the

film. Fluorine removal allows reconfiguration of bonds and diminishes the relaxation effect of strained bonds, resulting in increased intrinsic stress. The fact that fluo-

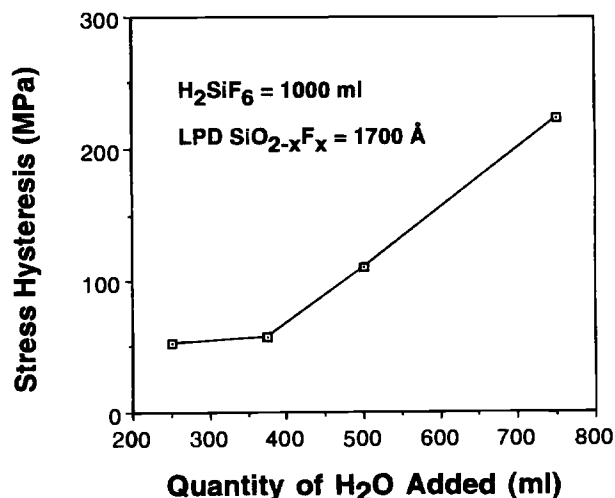


Fig. 3. Dependence of total stress hysteresis on the quantity of added H<sub>2</sub>O for 1700 Å thick LPD oxides. The hysteresis was calculated from the difference between initial stress measurements and final equilibrium stress measurements.

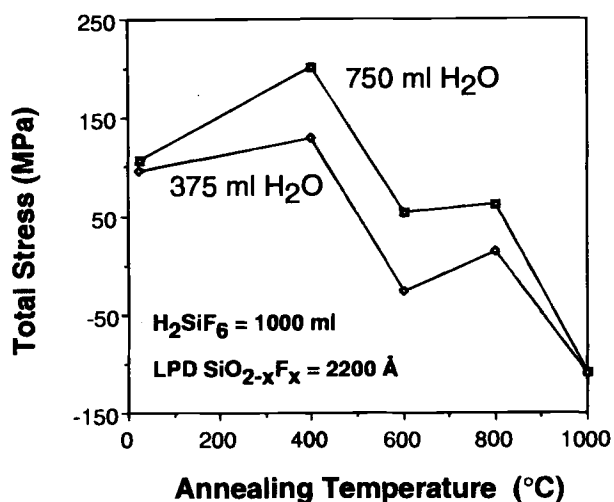


Fig. 4. Effects of *ex situ* thermal annealing temperature on total stress for 2200 Å thick LPD oxides. Two samples with different quantities of H<sub>2</sub>O added are shown for comparison.

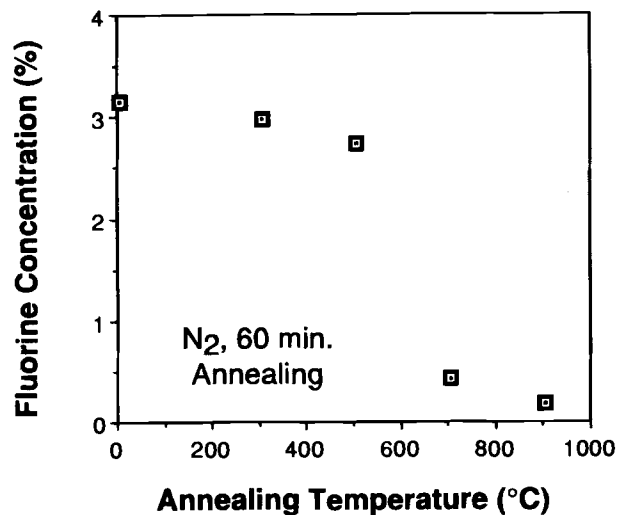


Fig. 6. Changes in fluorine concentration in LPD oxides annealed at different temperatures.

rine disappears from LPD oxide after annealing at 800°C has been confirmed by XPS spectra investigation. As shown in Fig. 6, fluorine concentrations in LPD oxides are greatly reduced after annealing over 700°C. As for annealing at 1000°C, the effect of strained bond relief diminishes stress further, and results in decreased stress.

The variations in total stress during *in situ* thermal cycling for LPD oxides with and without *ex situ* thermal annealing at 600°C were measured. As shown in Fig. 7, LPD oxide annealed at 600°C showed almost not hysteresis during *in situ* thermal cycling, but unannealed LPD oxide showed slight hysteresis. This can also be attributed to the buildup and release of intrinsic stress in the films. In films annealed at 600°C, few OH-related bonds exist, and the intrinsic stress is relieved. In this case, even when the film was subjected to *in situ* thermal cycling, no further densification and increase in strained bond occurred, thus the intrinsic stress remained constant during thermal cycling. That is, only thermal stress variations occurred and very little stress hysteresis was observed. A few OH-related bonds were still contained in the as-deposited LPD oxide, and consequently, hysteresis occurred during *in situ* thermal cycling.

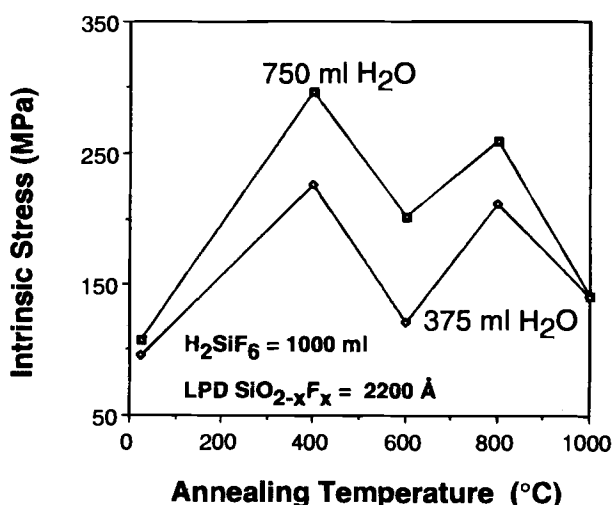


Fig. 5. Effects of *ex situ* thermal annealing temperature on intrinsic stress for 2200 Å thick LPD oxides. Two samples with different quantities of added H<sub>2</sub>O are shown for comparison.

### Conclusions

The effects of quantities of added H<sub>2</sub>O on stress in LPD oxides have been investigated. As-deposited LPD oxide film exhibited tensile stress as low as 83.3 MPa because of low-temperature deposition and fluorine incorporation. We also found that the less H<sub>2</sub>O was added, the lower the stress was. This can be attributed to the greater number of fluorine atoms incorporated in the film.

A hysteresis stress phenomenon was observed when the LPD oxide film was subjected to *in situ* thermal cycling. Films deposited with larger quantity of H<sub>2</sub>O added exhibited greater hysteresis because they contained more OH-related bonds. Thus, LPD oxide deposited with less added H<sub>2</sub>O will be more suitable for use as interlayer dielectrics in multilevel interconnections. In the case of *ex situ* thermal annealing, the intrinsic stress increased owing to the escape of OH (at 400°C) and the removal of F (at >600°C), while it decreased owing to bond strain relaxation (at 600°C and > 800°C). After annealing at around 600°C, the total stress is decreased to near 0 MPa.

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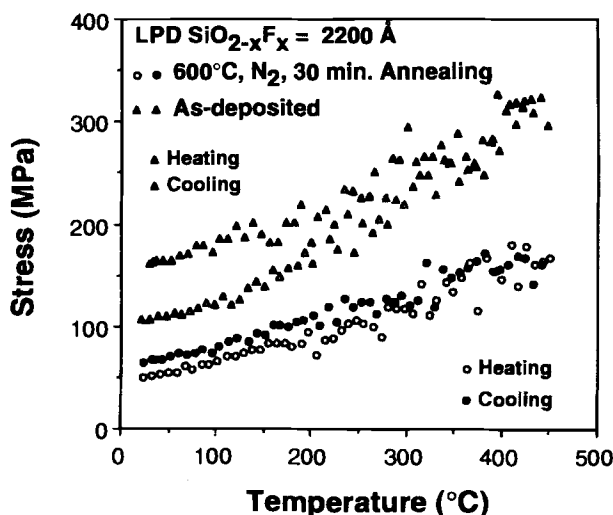


Fig. 7. Variations in total stress during *in situ* thermal cycling (25 ~ 450°C) for LPD oxides with and without thermal annealing at 600°C in N<sub>2</sub> for 30 min.

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#### REFERENCES

1. T. Homma, T. Katoh, Y. Yamada, and Y. Murao, *This Journal*, **140**, 2410 (1993).
2. S. Wolf, *Silicon Processing for VLSI Era*, Vol. 2, p. 195, Lattice Press, Sunset Beach, CA (1990).
3. D. Temple, A. Reisman, G. G. Fountain, M. Walters, and S. V. Hattangady, *This Journal*, **140**, 564 (1993).
4. T. D. Sullivan, *Appl. Phys. Lett.*, **55**, 2399 (1989).
5. K. Hinode, I. Asano, T. Ishiba, and Y. Homma, *J. Vac. Sci. Technol.*, **B8**, 495 (1990).
6. C. F. Yeh and C. L. Chen, *Semicond. Sci. Technol.*, **9**, 1250 (1994).
7. C. F. Yeh, T. Z. Yang, and T. J. Chen, *IEEE Trans. Electron Devices*, **ED-42**, 307 (1995).
8. C. F. Yeh, S. S. Lin, and T. Y. Hong, *IEEE Electron Device Lett.*, **EDL-16**, 316 (1995).
9. C. F. Yeh, C. L. Chen, and G. H. Lin, *This Journal*, **141**, 3177 (1994).
10. K. Ramkumar and A. N. Saxena, *ibid.*, **139**, 1437 (1992).
11. B. Bhushan, S. P. Muratka, and J. Gerlach, *J. Vac. Sci. Technol.*, **B8**, 1068 (1990).
12. L. M. Mack, A. Reisman, and P. K. Bhattacharya, *This Journal*, **136**, 3433 (1989).
13. K. Ramkumar, S. K. Ghosh, and A. N. Saxena, *ibid.*, **140**, 2669 (1993).
14. G. Smolinsky and T. P. H. F. Wendling, *ibid.*, **132**, 950 (1985).
15. M. Jarsoz, L. Kocsanyi, and J. Gibber, *Applications of Surface Science, 1982-1983*, p. 122 North Holland, Amsterdam (1983).
16. C. Blaauw, *J. Appl. Phys.*, **54**, 5064 (1983).
17. W. A. Pliskin and R. A. Gdula, in *Handbook on Semiconductors*, Vol. 3, T. S. Moss, Editor, p. 648, North-Holland Publishing Co., Amsterdam (1980).
18. M. Nakamura, R. Kanazawa, and K. Sakai, *This Journal*, **133**, 1167 (1986).
19. C. F. Yeh and C. L. Chen, *ibid.*, **142**, 3579 (1995).
20. D. Kouvatso, J. G. Huang, and R. J. Jaccodine, *ibid.*, **138**, 1752 (1991).
21. K. P. MacWilliams, L. F. Halle, and T. C. Zietlow, *IEEE Electron Device Lett.*, **EDL-11**, 3 (1990).
22. E. F. Dasilva, Y. Nishioka, and T. P. Ma, *IEEE Trans., Nucl. Sci.*, **NS-34**, 1190 (1987).
23. Y. Nishioka, K. Ohyu, Y. Ohji, N. Natuaki, K. Mukai, and T. P. Ma, *IEEE Electron Device Lett.*, **EDL-10**, 141 (1989).
24. S. Robles, E. Yieh, and B. C. Nguyen, *This Journal*, **142**, 580 (1995).
25. H. Sunami, Y. Itoh, and K. Sato, *J. Appl. Phys.*, **41**, 5115 (1970).

## Impurities in Chemical Bath Deposited CdS Films for Cu(In,Ga)Se<sub>2</sub> Solar Cells and Their Stability

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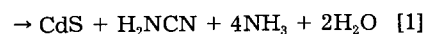
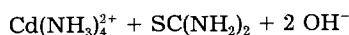
#### ABSTRACT

The highest efficiencies for Cu(In,Ga)Se<sub>2</sub>-based thin film solar cells have been achieved with CdS films prepared by a solution growth method known as the chemical bath deposition (CBD) technique. The impurity content in such cadmium sulfide films has been examined. By means of secondary ion mass spectroscopy, Fourier transform infrared spectroscopy, Rutherford backscattering spectrometry, and x-ray photoelectron spectroscopy, we conclude that CBD grown CdS films contain ~11 atom percent (a/o) O, ~5 a/o N as well as C and H. Unlike previously published results, cadmium carbonate (CdCO<sub>3</sub>) and water (H<sub>2</sub>O) are found to be the main oxygen-containing compounds. No clear evidence of cadmium hydroxide [Cd(OH)<sub>2</sub>] and/or oxide (CdO) is found. Carbon-nitrogen bonds originating from any pseudohalogenic ions [e.g., cyanamide (NCN<sup>2-</sup>), thiocyanate (SCN<sup>-</sup>), cyanate (OCN<sup>-</sup>), cyanide (CN<sup>-</sup>)] are identified as the main nitrogen impurity. To investigate the stability of the impurities, the films were subjected to air annealing (200 to 350°C) as well as storage (1.5 month) in three different environments: desiccator, humidity of 79%, and at 100°C. Air annealing results in a decrease of the water content, which disappears at 350°C. On exposure to humidity, the water content increases somewhat. The CN bonds are very sensitive to all treatments, but do not totally decompose, not even at 350°C. In contrast, CdCO<sub>3</sub> is much more stable.

#### Introduction

CdS is a superior photosensitive semiconductor. It has found extensive applications in the field of optoelectronics (e.g., solar cells, semiconductor lasers, photocells, photoconductive gas sensors, and infrared detectors). Thin films of this semiconducting material can be deposited by a variety of techniques, such as vacuum evaporation, sputtering, spray pyrolysis, chemical vapor deposition (CVD), and electrodeposition. A relatively less common method is a chemical solution growth technique known as chemical bath deposition (CBD).

In the CBD technique, the film deposition is carried out in an alkaline aqueous solution (pH > 10) containing thiourea [SC(NH<sub>2</sub>)<sub>2</sub>] and a cadmium complex [e.g., Cd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>]. When ammonia is used as the complexing agent, the overall reaction is assumed to be<sup>1-4</sup>



As an aqueous solution method, it presents many advantages: inexpensive, noncomplex equipment, low temperature (<100°C) and large-area deposition. All these properties are well suited for the manufacture of photovoltaic devices.

For CdTe/CdS and Cu(In,Ga)Se<sub>2</sub>/CdS/ZnO thin film solar cells, the chemical bath deposition shows another excellent property. The highest efficiencies for both these cell structures<sup>5-7</sup> have been achieved with CdS films prepared by this deposition technique.

The reason why CBD grown CdS gives a better photovoltaic performance as compared to, e.g., evaporated CdS remains unclear. It has been suggested that a pinhole-free conformal coverage, low temperature deposition, or chemical treatment of the surface during the CBD process are of importance, but clear evidence has not been submitted.

There exists, however, another possibility: impurities could be incorporated in the CdS film during the chemical

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