Novel low-stress $SiO_{2-x}F_x$ film deposited by room-temperature liquid-phase deposition method

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ABSTRACT

To develop a low-stress thin film for micromachined devices, a novel liquid-phase deposition (LPD) $SiO_{2-x}F_x$ technique utilizing silica-saturated H_2SiF_6 solution with H_2O addition only is proposed. Due to extremely low-temperature processing and fluorine incorporation, the stress of the LPD $SiO_{2-x}F_x$ film can be less than 100 MPa. In this paper, we found that the deposition parameter of H_2O addition has much effect on the stress of as-deposited LPD oxide. The stress variations with thermal cycling has also been clarified. We found that the LPD $SiO_{2-x}F_x$ film will be a good candidate as low-stress film for micromachined devices.

Keywords: low-stress, liquid phase deposition, $SiO_{2-x}F_x$

1. INTRODUCTION

The output characteristics of many micromachined and microfabricated devices are largely dependent on the mechanical stress of their constitution.[1] For example, in surface-micromachined sensors, the mechanical stresses are responsible for large bending, warping, and even fracture of thin film materials. Therefore, only low-stress thin films can be used in surface-micromachined devices. However, most thin films deposited at low temperature (300°C ~ 600°C) still have large residual stress (200 MPa ~ 300 MPa).[2,3] Thus, it is an important issue to develop a low-stress thin film for the micromachined and microfabricated devices.

Recently, a new oxide formation technology using the liquid phase deposition (LPD) method has been developed.[4] There are two main advantages for LPD $SiO_{2-x}F_x$ in comparison with other oxides. First, the substrate temperature during deposition can be greatly reduced to room-temperature. Since LPD oxide can be deposited at room-temperature,

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its stress is less than 100 MPa. Second, the fluorine atoms can be naturally incorporated into LPD oxide. These strongly suggest that LPD oxide technology is a potential candidate for applying to micromachined and microfabricated devices.

Until now, the detailed properties about the stress of LPD $SiO_{2-x}F_x$ was still unknown. In this paper, we will first investigate the influence of deposition parameter on the stress of LPD oxide. Because the change in LPD oxide microstructure with heat treatments often results into drifting in mechanical stress, next, the stress variation in LPD oxide with different thermal cycling will also be clarified.

2. EXPERIMENTAL METHODS

In preparing the aqueous solution for LPD oxide formation, 75 g of 99.99% pure silica (SiO_2) powder was added to 1750 ml of 4 mol/l hydrofluosilicic acid (H_2SiF_6). After being stirred at 23°C for 17 hours, the solution became saturated with silicic acid [$Si(OH)_4$]. Then the solution was filtered to remove the undissolved silica powder. To further make the solution become supersaturated with silicic acid for deposition, the deionized water (H_2O) ranged from 250 ml to 750 ml was added to the 1000 ml saturated solution.

P-type, (100), 10 ~ 20 Ω-cm, 4-inches silicon wafers were used as substrates in this experiment. The thin native oxides, naturally formed on the substrate surfaces in the HCl + H_2O + H_2O_2 mixed solution during initial cleaning, were reserved for LPD oxide deposition. The deposition temperature of 25°C was accurately controlled by a water bath. The thickness of LPD $SiO_{2-x}F_x$ was controlled by immersing time.

LPD Oxide stress was determined through measuring the radius of wafer curvature with a Tencor FLX-2320 thin film stress measurement instrument using a single laser reflection technique.[5] After deposition, the oxide layer on the back side of wafer was stripped using a 6:1 buffered HF solution. For each sample, the radii of wafer curvature were measured prior to LPD oxide deposition and following such deposition. The stress (σ) can be calculated from the changes in the radius of wafer curvature according to the following equation:

$$\sigma = \frac{E_s}{6(1-\nu_s)} \cdot \left(\frac{t_s^2}{t_f}\right) \cdot \left(\frac{1}{R_2} - \frac{1}{R_1}\right), \qquad (1)$$

where E_s and ν_s are the Young's modulus and Poisson's ratio of Si, t_f and t_s are the thickness of LPD oxide and Si wafer, R_2 and R_1 are the radii of wafer curvature with and without LPD oxide.

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The measurement of *in-situ* thermal-cycling stress measurement was performed with the above instrument. The stress instrument has additional arrangement in which a wafer with the deposited oxide can be heated in an N_2 atmosphere to the required temperature at a preset ramp rate (8.5°C/min), and then cooled to room temperature at a maximum cooling rate of 1.6°C/min. During heating and cooling, the stress was measured periodically.

In the measurement of *ex-situ* thermal-cycling stress, post-deposition heat-treatments were performed at 300 ~ 800°C in N_2 ambient for 1 hr. The wafer curvature was immediately measured after each of the heat-treatments. After the measurements of *ex-situ* thermal-cycling stress were completed, the oxide film was stripped from the substrate, and the bare wafer curvature was measured again to check whether plastic deformation of the silicon substrate occurred in the processing steps.[7, 8]

3. THIN FILM STRESS

In general, the total stress (σ_T) in thin film has two components, they are thermal stress (σ_{th}) and intrinsic stress (σ_{in}). That is,

$$\sigma_T = \sigma_{th} + \sigma_{in}. \tag{2}$$

The thermal stress component is attributed to that the difference in thermal expansion coefficients between the film and the substrate can cause differential contractions during cooling from the deposition temperature. σ_{th} can be given by[9]

$$\sigma_{th} = E_f / (1 - \nu_f) \int_{T_a}^{T_d} (\alpha_f - \alpha_s) dT, \tag{3}$$

where E_f is the Young's modulus of the film, ν_f is the Poisson's ratio of the film, α_s and α_f are the thermal expansion coefficients of the substrate and the film, respectively, and T_d and T_a are the deposition and the stress measurement temperature, respectively. For SiO_2 on Si, $E_f/(1-\nu_f) = 8.5 \times 10^{11}$ dynes/cm^2.[9] If it is assumed that α_s and α_f do not change with temperature, then the above equation can be simplified to

$$\sigma_{th} = \left(\frac{E_f}{1 - \nu_f}\right) \cdot (\alpha_f - \alpha_s) \cdot (T_d - T_a), \tag{4}$$

since α_s is larger than α_f for oxide film on Si,[10] and T_d is usually larger than T_a, the resulting thermal stress at room temperature becomes compressive. The intrinsic stress in the oxide film

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is caused owing to the bonds structure (bonding between Si, O, and OH). It can be either tensile or compressive.

4. RESULTS AND DISCUSSION

Fig. 1 shows the dependence of stress on H_2O quantity for the wafers with 320 nm-thick LPD $SiO_{2-x}F_x$. All the stresses were found to be in a state of tensile, and the magnitudes were in the range of 70 ~ 120 MPa. These values are much lower than that of 200 ~ 500 MPa in CVD oxides.[11-15] Since the deposition and the measurement temperatures are nearly the same, the stress mainly results from intrinsic stress. The intrinsic stress in LPD oxide results from the bond strains originating from the dehydration reaction during deposition. When the Si-O-Si bonding takes place after dehydration, there must be a large puckering strain.[16] If sufficient energy is not applied to the oxide, bond strains remain and result in intrinsic stress. Since dehydration reaction causes shrinkage of the film, the intrinsic stress should be tensile.[17]

The 320 nm-thick film deposited with 250 ml H_2O shows a stress of 72 MPa, but both the same-thickness films deposited with 500 ml and 750 ml H_2O show a rising stress to 112 MPa. In our previous studies,[6] we have shown that the fluorine atoms can be naturally incorporated into the LPD oxide during deposition. And the less the H_2O quantity added, the more the fluorine atoms incorporated into the LPD oxide. Thus, for the film deposited with 250 ml H_2O the lower stress (72 MPa) can be attributed to the more fluorine incorporation in the film. This is consistent with the hypothesis that fluorine incorporation results in strain relaxation.[18-20] The interaction between a fluorine atom and a strained Si-O bond will generate a Si-F bond and a nonbridging oxygen bond, and result in a local strain relaxation and thereby a stress reduction.[21]

According to the above discussion, the stress of LPD oxide prepared with 750 ml H_2O added should be larger than that prepared with 500 ml H_2O added because of less fluorine atoms incorporated in the former. However, in Fig. 1, we found that there is only a little difference in stress between the two samples. For LPD oxide prepared with 750 ml H_2O, the less increase may be due to more OH contained in the film.[22, 23] After H_2O has been added to a saturated H_2SiF_6 solution, the intermediate polysilicic acids will be formed by the polymerization of the silicic monomer $Si(OH)_4$, and then absorbed onto the substrate surface.[6] Acid-catalytic dehydration occurs between these absorbed polysilicic acids, followed by Si-O-Si bond formation. The larger the H_2O quantity added, the faster the polysilicic acid formed and absorbed onto the substrate surface. In that case, the dehydration

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reaction cannot be completely finished in time, and a large amount of residual Si-OH bonds remain in the film, thus make stress less increase.

The effects of *in-situ* thermal cycling on the total stress for LPD oxide were measured and shown in Fig. 2. During the heating, the total stress tends to become more tensile with increasing temperature. During the cooling, the total stress becomes less tensile with decreasing temperature. The final value of total stress is larger than the initial value, and the total stress variation shows a hysteresis. As mentioned above, a total stress in thin film during thermal cycling includes two components: thermal stress and intrinsic stress. According to Eq. (4), the thermal stress will show a linear relationship with temperature. With increasing temperature, the thermal stress will become more tensile. However, during the cooling, the thermal stress will become less tensile. If there is no intrinsic stress, the variation of total stress during thermal cycling should follow the linear variation of thermal stress only, and show no hysteresis. However, from the hysteresis as shown in Fig. 2, it is believed that the LPD oxide has some amount of intrinsic stress.

The variation of intrinsic stress during the thermal cycling is determined by the changes in the oxide structure, especially the escape of OH, formation of additional Si-O-Si bonds, and then reconfiguration of these bonds. The annealing at a higher temperature will promote the escape of OH out of LPD film and the formation of Si-O-Si bonds. As mentioned in the handbook,[16] the Si-O-Si bonds formation can give rise to a large amount of bond strains. If a bond strain is not relieved, it will result in an intrinsic tensile stress in the film. Therefore, with increasing temperature, an increasing tensile intrinsic stress is developed in the oxide, and the total stress becomes more and more tensile. If a large intrinsic tensile stress is left in the film at the beginning of cooling, it will remain constant with decreasing temperature.[2] Thus, the total stress variation during the cooling exhibits larger than that during the heating, and a hysteresis occurs.

Fig. 3 shows the dependence of total stress on temperature in the case of *ex-situ* thermal cycling for the LPD oxide (234 nm) deposited with 250 ml H_2O. After an *ex-situ* annealing at 600°C, the total stress can drastically decrease from 80 MPa (tensile) to 4 MPa (compressive). The figure shows great difference in comparison with that of the sample with *in-situ* thermal cycling. To study the relationship of stress variation with the bonding structure, the variation of intrinsic stress (σ_{in}) with temperature, as shown in Fig. 4 was obtained by subtracting the calculated thermal stress (σ_{th}) from the total stress (σ_T).

The increasing of intrinsic stress after 1 hr thermal annealing in ~300°C is due to the escape of OH and reconfiguration of structure bonds as mentioned previously. However, after

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annealing at a higher temperature (400°C ~ 600°C) the intrinsic stress decreases a little. This is not only because the high-temperature annealing can make the silicon and the oxygen atoms in the oxide restructure and thereby result in reconfiguration of the Si-O-Si bonds, but also will relieve the bond strains and decrease the intrinsic tensile stress.[3] Therefore, there seems to exist a threshold temperature (400°C), beyond which the tensile intrinsic stress of the film will decrease. If the annealing temperature is over 600°C, we found that the intrinsic stress tends to become more tensile again. It can be attributed to the removal of fluorine atoms in the film owing to high-temperature annealing. As discussed above, the removal of fluorine will make strain bonds relaxation disappear and resultantly increase intrinsic stress. Fig. 5 shows the typical XPS spectra for the annealed LPD oxides at different temperature. The disappearance of F_{1s} peak indeed confirms that the annealing at 600°C ~ 800°C has removed the fluorine atoms from the film.

5. CONCLUSIONS

A novel low-stress LPD $SiO_{2-x}F_x$ technique utilizing silica-saturated H_2SiF_6 solution with H_2O addition only has been developed. The stress of as-deposited LPD $SiO_{2-x}F_x$ film is tensile, and can be less than 100 MPa because of low-temperature processing and fluorine incorporation. If an LPD oxide is deposited with less H_2O quantity, the film stress can become much lower due to more fluorine atoms incorporated in the film. A hysteresis phenomena of stress can be observed for the LPD oxide with *in-situ* thermal-anneal cycling. In the case of *ex-situ* thermal annealing, the intrinsic stress will increase owing to the removal of OH (~ 300°C) and the removal of F (> 600°C), but will decrease owing to the strain bonds relaxation (400°C ~ 600°C). The stress can decrease as low as 4 MPa (compressive).

6. ACKNOWLEDGMENT

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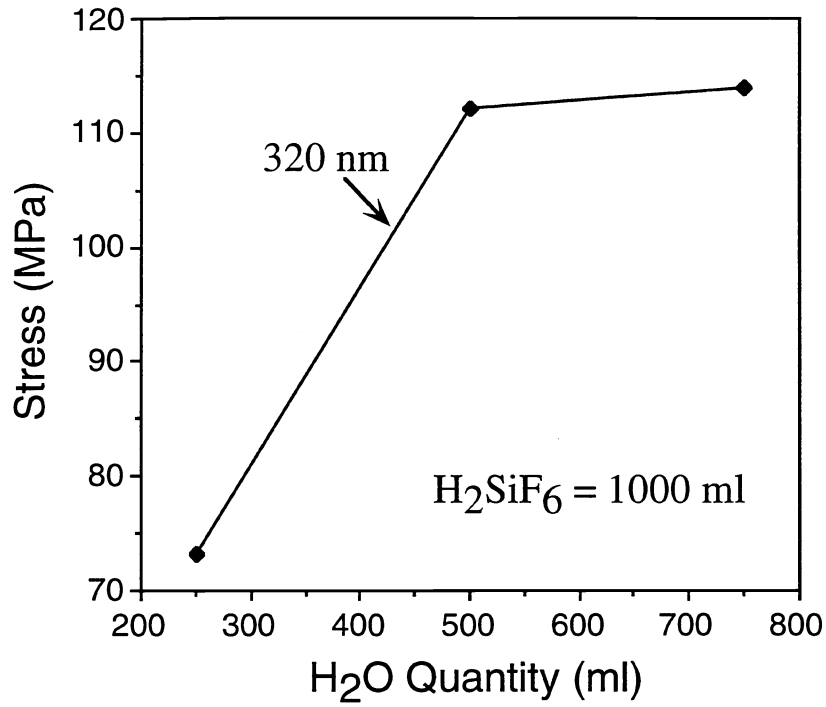

Fig. 1. Dependence of stress on H_2O quantity for 320 nm-thick LPD oxides

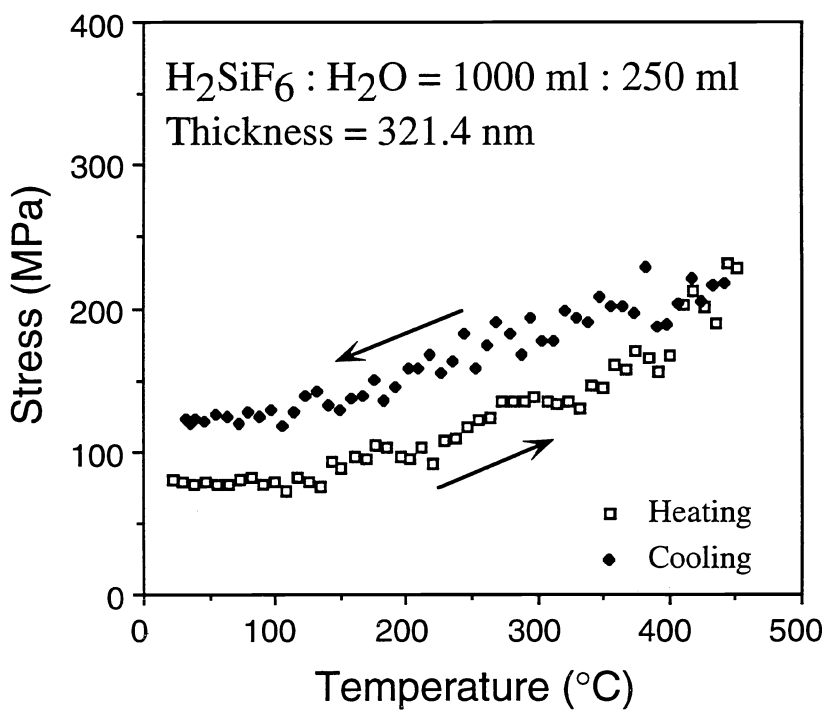

Fig. 2. Variation of total stress for LPD oixde during *in-situ* thermal cycling.

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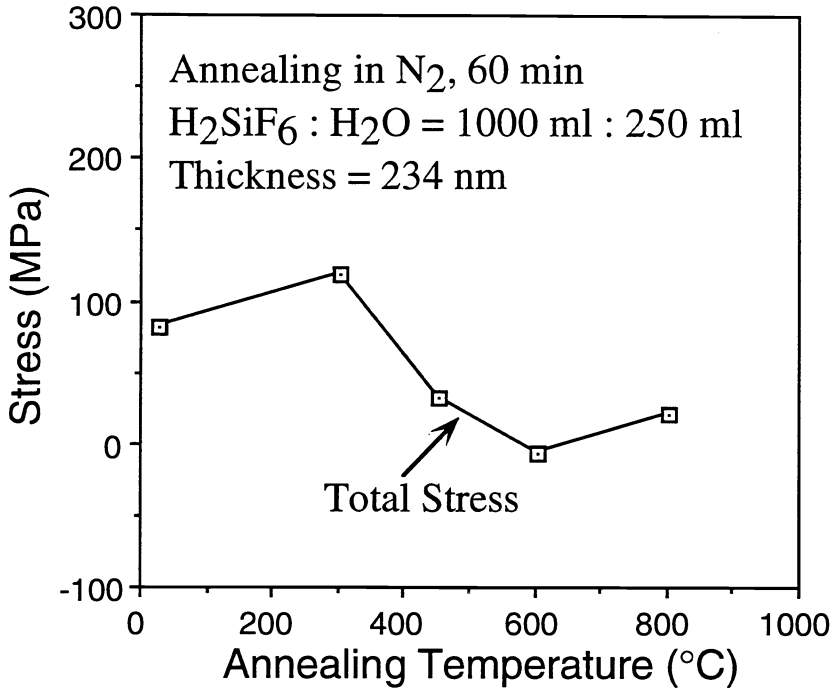

Fig. 3. Effects of *ex-situ* thermal annealing temperature on total stress for 234 nm LPD oxide.

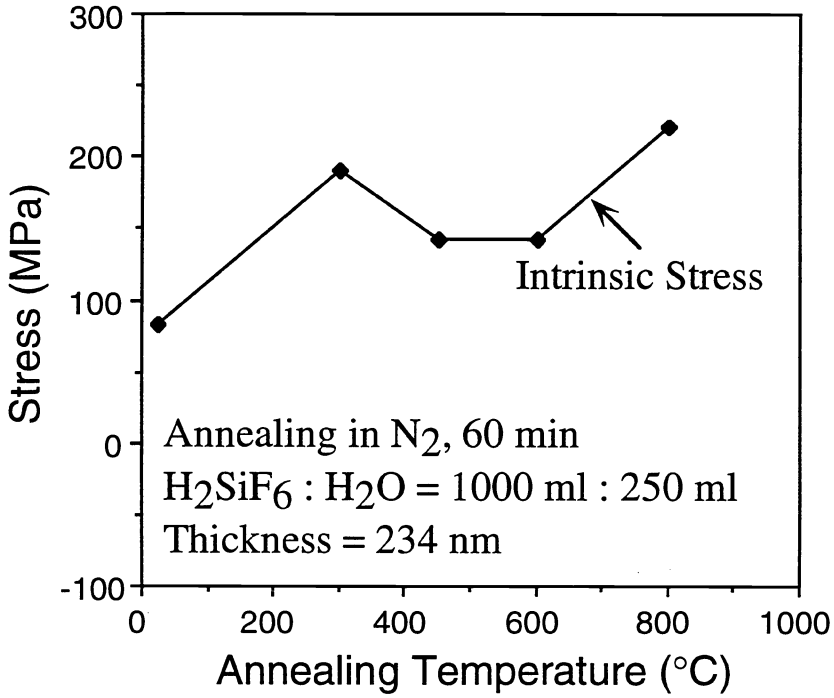

Fig. 4. Effects of *ex-situ* thermal annealing temperature on intrinsic stress for 234 nm LPD oxide.

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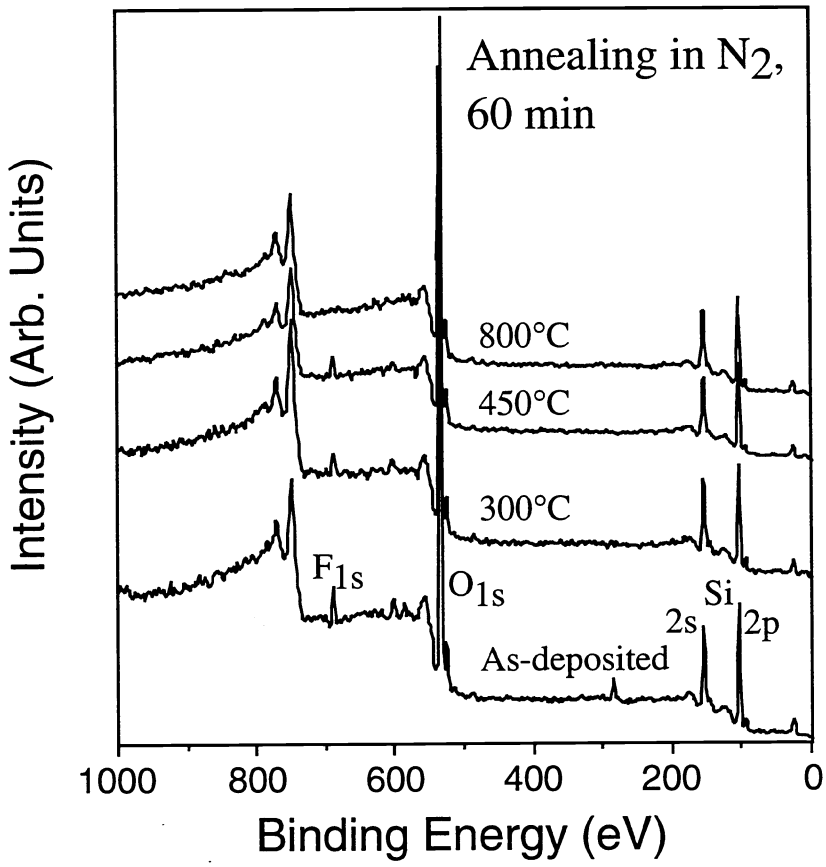

Fig. 5. XPS spectra for LPD oxides with *ex-situ* thermal annealing at different temperature.

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