# Effect of W Film Stress on W-Gate MOS Characteristics

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The fixed oxide charge density  $(N_r)$  in W-gate MOS capacitors was investigated as a function of both annealing temperature and stress in W film as deposited (initial stress). The initial stress was varied with two methods. One is sputtering at various Ar pressures. The other is depositing CVD-W with tensile stress on sputtered-W with compressive stress. It has been found that  $N_r$  greatly increases after 1000 °C annealing when the initial stress is more than  $5\times10^9$  dyne/cm<sup>2</sup> (compressive). It is supposed that the increase of  $N_r$  is due to Si defects formed at the Si-SiO<sub>2</sub> interface by the large stress of W film. On the other hand, when the initial stress was less than about  $5\times10^9$  dyne/cm<sup>2</sup> (compressive or tensile), the  $N_r$  value is as low as that for poly-Si up to 1000 °C annealing.

#### 1.INTRODUCTION

Tungsten (W) has been investigated for gate electrode of MOSFETs because of its low resistivity and its work function near the Sputtering method has been Si midgap. commonly used to deposit W film on SiO2. In general, sputtered-W shows good characteristics as MOS gate electrode 1-2), but in some cases it seems to degrade MOS characteristics due to its large stress. We reported<sup>3)</sup> previously that the fixed oxide charge density (N<sub>f</sub>) of sputtered-W gate MOS capacitors increases greatly with annealing in inert ambient at a high temperature ranging from 900 °C to 1000 °C but Nr of Laser CVD-W gate ones is not the case. The stress as deposited (initial stress) in Laser CVD-W film is less than 1×10<sup>9</sup> dyne/cm<sup>2</sup>, but that in sputtered-W is 1x10<sup>10</sup> dyne/cm<sup>2</sup>. Hence, it may be expected a relation between  $N_f$  and W film stress. Yamamoto et al.4) reported that pre-annealing of W before gate patterning is important and the degradation of gm MOSFETs under high drain voltage of operation is enhanced if without this preannealing. They assigned the origin of this effect as the stress of W-gate which is

concentrated at the edge of gate and induces defects near the gate edge in Si. Other authors 5-6 also reported the effect of the mechanical stress induced by gate electrodes or passivation films on the degradation of MOS characteristics in the case of  $\gamma$ -ray irradiation or hot electron injection.

The purpose of this study is to investigate the effect of W film stress on the characteristics, particularly fixed oxide charge density, of W-gate MOS capacitor after annealing.

#### 2.EXPERIMENTAL

MOS capacitors with W gates were fabricated on (100) oriented p-type silicon wafers (3Ω·cm). After LOCOS isolation, 80 nm-thick gate oxide was formed. By dipping in HF solution from the edge of a wafer, various thicknesses of oxide (10 - 80 nm) were obtained across a wafer. 300 nm-thick W film was deposited on this wafer by two sputtering and W-CVD after methods, sputtering. Sputtered-W was deposited at various Ar pressures from 5 to 20 mTorr. The W taget purity is 99.995 %. CVD-W was deposited on sputtered-W using WF6 and H2

gases at 400 °C. For preventing oxidation of W and contamination from photo-resist, 200 nm-thick silicate glass were deposited onto W. Then these samples were annealed at a higher temperature than 800 °C in N<sub>2</sub> for 30 min. Next, W gates were patterned by dry etching. Finally these samples were annealed in H<sub>2</sub> at 450 °C for 30 min.

The characteristics of MOS capacitors were evaluated by C-V method. The stress of W film was calculated from the carvature of a non-patterned 5 inch Si wafer.

## 3. RESULTS AND DISCUSSION

Fig.1 shows the variation of W film stress with the annealing temperature for samples having various initial stresses. The initial stresses were varied from high compressive to low compressive by changing Ar pressure at sputtering.") For the all samples, the stress decreases with increasing temperature. After 1000 C annealing, the stress changes from compressive to tensile and, regardless of the values of initial stress, is converged to a fixed value which corresponds to the thermal residual stress of W<sup>8</sup>).



Fig.1 Variation of W film stress with annealing temperature for samples having various initial stresses

Fig.2 shows the dependence of Nr on annealing temperature. N<sub>f</sub> was calculated from the relation between flatband voltage  $(V_{\rm FB})$  and gate oxide thickness  $(T_{\rm ox})$  in a wafer, as shown in Fig.2. After annealing at a temperature lower than 900 °C, Nr is as low as that for poly-Si gate and independent of Ar at pressure sputtering (PAr). However, after annealing at 1000 °C, Nr for W films sputtered at 5 and 12 mTorr increases abruptly. Fig.3 shows the relation between Nf after annealing at 1000 °C and the initial It is found that N<sub>f</sub> greatly instress. creases with increasing the initial stress.

If this increase of  $N_r$  is induced by the sputtering damage to gate oxide, which depends on  $P_{Ar}$ , the effect of stress can not be separated from that of sputtering damage in the case of controlling the initial stress by means of varying  $P_{Ar}$ . For this reason, the initial stress was controlled by means of the depositing CVD-W with tensile stress on sputtered-W with compressive one. Sputtered-W was deposited at 5 mTorr because the  $N_r$  value after 1000 °C annealing was largest as described before.



Fig.2 Dependence of fixed oxide charge density  $(N_f)$  on annealing temperature, and relation between flatband voltage  $(V_{\rm FB})$  and gate oxide thickness  $(T_{\rm ox})$ 





The dependence of the initial stress in CVD-W/Sputtered-W (two-layer W) film on sputtered-W thickness is shown in Fig.4. The initial stress in two-layer W film was varied by changing the ratio of sputtered-W and CVD-W thickness being kept the thickness of two-layer W film at 300 nm. The initial stress decreases with decreasing sputtered-W thickness and finally changed from compressive to tensile.

Fig.4 also shows the relation between N<sub>f</sub> after annealing at 1000  $\ensuremath{\mathbb{T}}$  and the initial stress in two-layer W film. For this twolayer W film with stress lower than 5x10°  $dyne/cm^2$  (tensile or compressive), the  $N_f$ value did not increase after 1000 °C annealing. This result is similar to that for sputtered-W shown in Fig.3. These facts indicate that the increase of N<sub>f</sub> after 1000  $\mathcal C$  annealing is not induced by the damage to the gate oxide at sputtering.

Previous studies have shown<sup>9-11)</sup> that  $N_f$  decreases on annealing in inert ambient. Akinwande et al.<sup>10)</sup> reported that  $N_f$  exponentially decreases with time and saturates to a steady-state value after annealing, at 1000 °C for 10 min, and that this steady-



Fig.4 Relation between fixed oxide charge density  $(N_r)$  after annealing at 1000 °C and initial stress in CVD-W/sputtered-W film, and dependence of initial stress in that film on sputtered-W thickness.  $\bigcirc$  : CVD-W/sputtered-W,  $\bigcirc$  : sputtered-W

state value decreases with increase in temperature. However, in our experiment, when the initial stress is larger than  $5\times10^9$  dyne /cm<sup>2</sup> (compressive), N<sub>f</sub> increased greatly after 1000 °C annealing in spite of annealing time of 30 min, as shown in Figs.3 and 4. It is cosidered that, in our experiment, N<sub>f</sub> is induced by another origin which is different from that previously reported<sup>10-11</sup>.

We suppose that the large increase of N, observed for some samples after 1000 °C annealing is due to Si defects formed at Si-SiO<sub>2</sub> interface. The stress of W film seems to be released after 1000 °C annealing so far as measuring the carvature of Si wafers, but what happens at the interfaces of W-SiO, and SiO2-Si is not clear. The creep of W itself is one of the origins which induce the relaxation of the stress, but the viscoelastic flow of  $SiO_2^{12}$  may be the main origin. In the case that the initial stress is large, defects, perhaps vacancies or dislocations, may be formed additionally at the Si-SiO<sub>2</sub> interface because there exists high tensile



Fig.5 Variation of work function difference ( $\phi$  ms) with annealing temperature

stress. These vacancies or dislocations in Si may not recover completely after 1000  $\ensuremath{\mathbb{C}}$  annealing, as a result, N\_r increases after 1000  $\ensuremath{\mathbb{C}}$  annealing.

Finally, the variation of work function difference ( $\phi$  ms) with annealing temperature is shown in Fig.5.  $\phi$  ms for W sputtered at 12 and 20 mTorr becomes a constant value after annealing a temperature ranging from 800 °C to 1000 °C. The work function ( $\phi$  m) of W calculated from this  $\phi$  ms value is 4.9 eV. The work functions of W for various face orientations are different.<sup>13)</sup> For instance , the values for (100), (112), and (110) faces are 4.57 - 4.67, 4.89 - 5.24, and 5.05 respectively. - 5.30 eV, From X-ray diffraction measurements, the (110) face orientation dominated in these W films in both cases before and after annealing.  $\phi$  m obtained by our experiments are lower than the reported value for the (110) face. It is considered that the difference is caused by the fact that W film is polycrystaline in this experiment. The difference between  $\phi$  ms before and after annealing suggests that the structure at the W-SiO<sub>2</sub> interface changes with annealing process. However, these results indicate that  $\phi$  m is stable for low stress W film after annealing at a temperature higher than 800 °C.

## 4.CONCLUSION

The fixed oxide charge density  $(N_f)$  in W-gate MOS capacitor was investigated as a function of both the initial stress in W film and the annealing temperature. When the initial stress is higher than 5×10° dyne /cm<sup>2</sup> (compressive), the N<sub>f</sub> value greatly increases after 1000 °C annealing. It is supposed that the increase of  $N_f$  is due to Si defects formed at the Si-SiO<sub>2</sub> interface by the large stress of W film. On the other hand, when the initial stress is less than  $5\times10^{9}$  dyne/cm<sup>2</sup> (compressive or tensile), the N<sub>f</sub> value is as low as that for poly-Si up to 1000 ° annealing. The work function of this low stress W is 4.9 eV after annealing above 800 °C. For reducing the initial stress in W film, the following methods are effective. One is sputtering at high Ar pressure (about 20 mTorr). The other is the depositing CVD-W with tensile stress on sputtered-W with compressive stress. Both the above methods are quite useful for obtaining stable W-gate MOS capacitors.

### REFFERENCES

- 1) N.Kasai et al.; IEDM Tech.Dig. (1988) 243.
- B.Davari et al.; 1987 Symp. on VLSI Tech. Dig. (1987) 61.
- H.Matsuhashi et al.; Jpn.J.Appl.Phys., <u>27</u> (1988) L2161.
- N.Yamamoto et al.; IEEE Trans.Electron Devices, ED-34 (1987) 607.
- 5) K.Kasama et al.; IEEE Trans.Nucl.Sci., NS-34 (1987) 1202.
- J.Mitsuhashi et al.; IEDM Tech.Dig. (1986) 386.
- 7) N.Yamamoto et al.; J.Electrochem.Soc., <u>133</u> (1986) 401.
- 8) R.C.Sun et al.; J.Appl.Phys, 44(1973) 1009.
- 9) R.R.Razouk et al.; J.Electrochem.Soc., <u>126</u> (1979) 1573.
- 10) A.I.Akinwande et al.; J.Electrochem.Soc., 134 (1987) 2565.
- 11) A.I.Akinwande et al.; J.Electrochem.Soc., <u>134</u> (1987) 2573.
- 12) E.P.Eernisse; Appl.Phys.Lett, 30(1977) 290
- 13) T.V.Vorburger et al.; Surface Sci., <u>48</u> (1975) 417.

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