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Ultra-Low-Temperature Growth of High-Integrity Thin Gate Oxide Films by Low-Energy Ion-Assisted Oxidation

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High integrity thin gate oxide films have been grown at a temperature as low as 450 °C by direct oxidation of silicon. The bombardment of the silicon surface by low energy ions of argon and oxygen mixed plasma is utilized to activate the oxidation process. Dielectric breakdown field intensity of the oxide film of 12 MV/cm is obtained by the MOS capacitor evaluation. The precise control of the bombarding ion energy is essential in achieving the high integrity thin gate oxide films.

1. INTRODUCTION

Extensive studies have been reported on the low temperature growth of silicon gate oxide films using a variety of methods;
e.g., sputter deposition[1],[2], silicon oxidation in oxygen plasma[3], thermal oxidation[4], chemical vapor deposition[5] and liquid phase deposition[6].

The purpose of this study is to develop a gate oxidation process by which high integrity gate oxide films are grown at a temperature as low as 450 °C, using low energy argon ion-assisted oxidation technology.

2. EXPERIMENTAL

Fig.1 illustrates a dual-frequency-excitation plasma processing equipment used in this experiment, which has a plasma excitation electrode at the upper position and a wafer mount electrode at the lower position of the plasma process chamber. By choosing optimum frequency and power supplied to these electrodes, the independent and precise control of ion bombardment energy and ion flux density for wafer surface activation is achieved.

The wafer is fixed on the electrode mount by means of an electrostatic chuck and oxidation process is carried out in argon/oxygen mixed plasma with simultaneous heating of the wafer by the electric heater equipped in the wafer electrode.

Prior to oxidation the chemical oxide[8] was formed of a thickness of 0.8 to 0.9 nm by H_2O_2 dipping for 10 minutes at 85 °C to prevent native oxide growth. The oxide film thickness was measured by XPS. Electrical properties of the grown oxide films were evaluated in terms of MOS ($Al/SiO_2/n\text{-}Si(100)$) capacitor of 1.69×10^{-4} cm^2 in area.

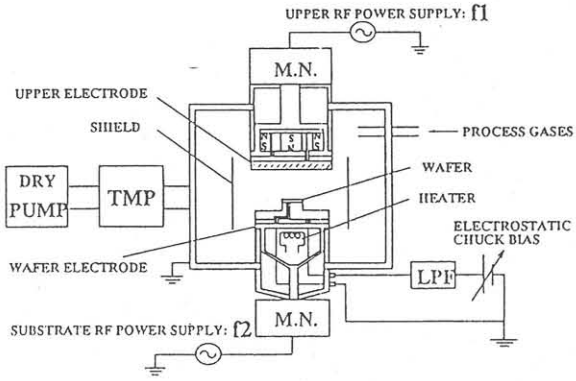

Fig.1 Schematic of dual-frequency-excitation plasma process equipment.

3. RESULTS AND DISCUSSION

3.1 Dielectric Breakdown Voltages of the MOS Capacitors

Fig.2 shows the dielectric breakdown field intensity histograms of MOS ($Al/SiO_2/n$-Si(100)) capacitors for the low-energy ion-assisted oxide (Fig.2(a)) and the dry oxide at 1000 °C (Fig.2(b)). Dielectric breakdown field of 12 MV/cm is achieved by the 450 °C oxidation. The low-energy ion-assisted oxidation exhibits a comparable dielectric field intensity distribution to that of the thermal oxidation.

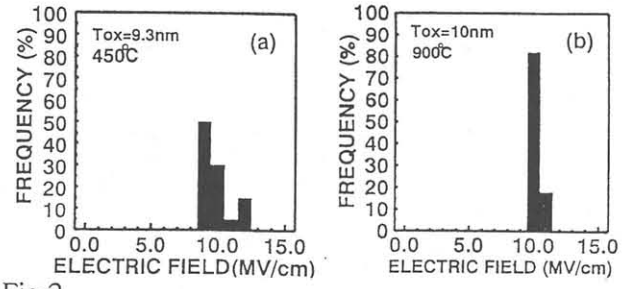

Fig.2

Dielectric breakdown characteristics of low-energy ion-assisted oxide (a) and thermal oxide (b). Electrode area is $1.69 \times 10^{-4} cm^2$. Judgment current is $1.0 \times 10^{-4} A$.

3.2 Assisting Effect of Argon Ion in the Oxide Growth

Fig.3 shows the comparison of the dielectric breakdown characteristics of the MOS capacitors formed by (a) argon and oxygen mixed gas plasma in the mixing ratio of 300 sccm and 8 sccm, respectively, and (b) 100 % oxygen plasma. Higher breakdown field intensity is observed in the histogram (a) than in (b). This fact implies that argon ions play an essential role in improving the dielectric field intensity of the oxide film.

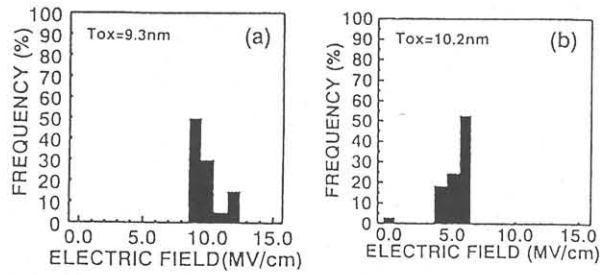

Fig. 3

Dielectric breakdown characteristics of Ar/O_2 plasma oxide and O_2 plasma oxide at 450°C. Electrode area is $1.69 \times 10^{-4} cm^2$. Judgment current is $1.0 \times 10^{-4} A$.

3.3 Oxidation Time Dependence of the Film Growth

Fig.4 gives the time dependence of the low-energy ion-assisted oxide thickness. Two evidently different types of film growth modes are observed, an earlier stage from the beginning to the first 10 minutes of oxidizing with the growth rate of relatively high speed, 0.73 Å/min and the subsequent stage with the growth rate of slower speed, 0.28 Å/min.

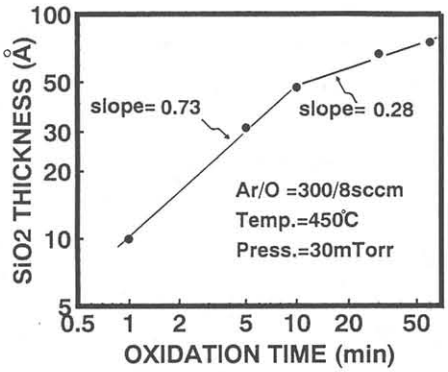

Fig. 4

Oxide thickness as a function of low-energy ion-assisted oxidation time at 450°C.

The low energy ions presumably create sort of point defects in the oxide film for a limited relaxation time, by giving the kinetic energy of bombardment, simultaneously supported by the thermal energy from the wafer heater. The local disturbance of lattice energy from the steady state caused by the pseudo-defects allows to diffuse the oxidizing species to the oxide-silicon interface during the limited lattice relaxation time, which determines the depth of the oxidizing species diffusion.

3.4 Damaging Action of High Energy Ions on the Oxide Film Surface

Oxide films were grown by three different bombarding energies, 9, 14 and 19 eV, remaining other process parameters identical.

Fig.5 indicates the dielectric breakdown field intensity distributions as a function of bombarding ion energy. The maximum distribution frequency shifts to higher range as ion energy is reduced from 19 eV to 9 eV.

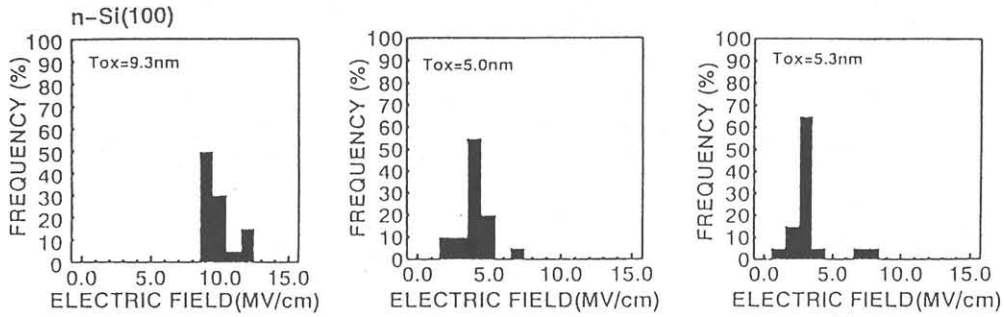

Fig.5 Dielectric breakdown characteristics of low-energy ion-assisted oxide as a function of ion bombardment energy onto wafer surfaces. Such various energies (Eion=9eV (a), 14eV (b), 19eV (c)) were obtained by changing the input of substrate RF power.

From these results it is concluded that the precise control of the bombarding ion energy is quite essential in the low-energy ion-assisted oxidation, since the argon ions tend etch the oxide surface again as their bombarding energy is increased.

3.5 Activation Energy of Argon Ion-Assisted Oxidation

The plot of the oxide thickness against the reciprocal of temperature is given in Fig.6. The oxidation time was fixed to 10 minutes and the wafer temperature was changed from 100 °C to 430 °C. Other process parameters are given in the figure. The activation energy of ion-assisted oxide calculated from this plot is 0.025 eV. This value is much smaller than the activation energy, 1.54 eV, of thermal oxidation. This fact implies that the oxidation is dominantly activated by the ion bombardment, which supports the discussion related to the previous experimental results.

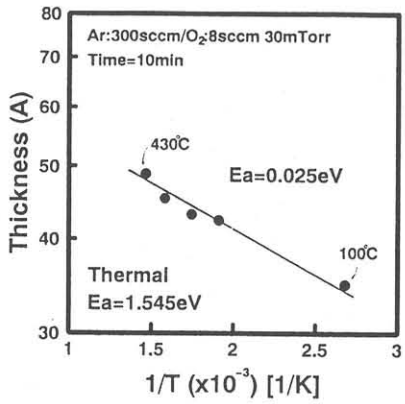

Fig.6 Arrhenius plot of oxide thickness. Oxidation time is 10 minutes.

4. CONCLUSION

A gate oxide film was obtained of about 10 nm thick having almost equivalent dielectric breakdown field intensity with that of thermal oxide by means of the low-energy ion-assisted oxidation using a dual-frequency-excitation plasma processing equippment.

The precise control of the bombarding ion energy is most important to obtain a high integrity thin gate oxide film in the low-energy ion-assisted oxidation.

5. ACKNOWLEDGMENTS

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