Low Temperature Deposition of High Quality Silicon Oxide Films

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The electrical properties of SiO_2 films deposited at low temperature below 600° with ECRCVD, Sputter and APCVD were compared with those of Th- SiO_2 film. The film of ECRCVD- SiO_2 deposited without substrate heating had a low density of interface state in MOS capacitor. Its density was 3.2×10^{10} (cm⁻² eV⁻¹) near the Si mid-gap. It was convinced that the ECRCVD was one of the promising methods for high-quality SiO_2 -film deposition at low temperature.

1.INTRODUCTION

It is said that a liquid crystal display is the most promising candidate of future display in 1990's. The fabrication of large-area TFT on inexpensive glass substrates is a key technology for liquid crystal display. Accordingly, the maximum temperature of TFT fabrication processes should be below a glass strain point of 600°C.

Recently, deposition processes of SiO₂ films at low temperature with ECR-plasma-CVD (ECRCVD) method¹⁾⁻⁵⁾,Sputter (SP) method⁶⁾⁻⁷⁾ and Plasma-CVD method⁸⁾ has been studied. In particular, the quality of SiO₂ films was improved below 200°C by ECRCVD method and SP method. However, the low temperature deposition method has not been well established in fabricating gate insulator films with good electrical properties which are comparable to those of thermal SiO₂.

In this paper, the optical, chemical and electrical properties of $ECRCVD-SiO_2$ is discussed in comparison with those of SiO_2 films formed with SP, APCVD and Thermal oxidation(Th) methods.

2.EXPERIMENTAL PROCEDURE

Silicon oxide films were deposited with ECRCVD, SP, APCVD method, respectively. Typical conditions of each deposition method are shown in Table 1. The films were formed on P-type single crystal silicon wafers. Etching rate with buffered HF solution (HF content 5%, at 25 °C) and refractive index were measured. The MOS capacitors were fabricated on P-type (100),10~150 cm silicon wafers with a 1000Å thick gate insulator, and a 0.005 cm² aluminum gate electrode. Finally, those samples were postmetallization-annealed in N₂ at 400° for 40 min..

The current density-field strength (J-E) characteristics were measured using MOS capacitors by applying negative voltage to the aluminum gate electrode. The quasistatic C-V characteristics were also measured using MOS capacitors. The interface state density was calculated by using the quasi-static C-V curves⁹⁾. The properties of films were evaluated by comparing with those of Th-SiO₂ fabricated by dry oxidation at 1000 \degree .

Table 1 Deposition Conditions

ECR-plasma-CVD method

Reactant gases	O_2 and SiH ₄
Gas flow rate ratio	$0.33 (SiH_4/O_2)$
Gas pressure	1.5 mTorr
Microwave power	300 W
Substrate temperature	25 - 600℃

Sputter method (RF magnetron sputter)

Target	SiO_2 (6N)
Sputtering gas	Ar and O_2
Gas flow rate ratio	$0.43 (0_2 / Ar)$
Gas pressure	5 mTorr
RF power	800 W
Substrate temperature	25 - 300 r

Atmospheric pressure CVD method

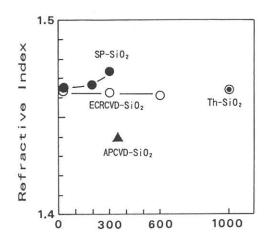
Reactant gases	SiH_4 and O_2
Substrate temperature	350 C

3.RESULTS AND DISCUSSIONS

The thickness unifirmity of films is less than $\pm 6\%$ on wafer (diameter: 100mm)in each deposition. Refractive index of SiO₂ films as a function of deposition temperature is shown in Fig. 1. Refractive indexes of both ECRCVD-SiO₂ and SP-SiO₂ were comparable to that of Th-SiO₂.

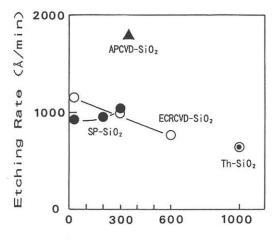
Chemical etching rates of SiO₂ films is shown in Fig. 2 as a function of deposition temperature. Etching rates of both ECRCVD-SiO₂ and SP-SiO₂ were farely lower than that of APCVD-SiO₂. The film of ECRCVD-SiO₂ had as low etching rate as that of Th-SiO₂ in high temperature region around 600°C. It was suggested that ECRCVD-SiO₂ and SP-SiO₂ deposited at low temperature were very dense films in comparison with APCVD SiO₂ films.

Breakdown field of SiO_2 films vs. deposition temperature is shown in Fig. 3. In low temperature region (R.T.~300°), all



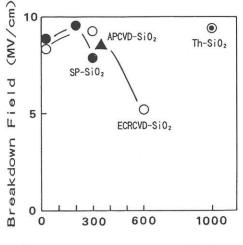
Deposition Temperature (°C)

Fig.1 Refractive index of SiO_2 films as a function of deposition temperature.



Deposition Temperature (°C)

Fig.2 Etching rate of SiO_2 films as a function of deposition temperature.



Deposition Temperature (°C)

Fig.3 Breakdown field of MOS capacitors using SiO_2 films vs. deposition temperature.

of ECRCVD-SiO₂, SP-SiO₂ and APCVD-SiO₂ films had rather high breakdown field which was comparable to that of Th-SiO₂.

Figure 4 shows that the J-E characteristics of MOS capacitors using SiO_2 films formed under the following.

- Th-SiO₂ :dry oxidation at 1000°.
- ECRCVD-SiO₂ :deposited with ECRCVD method without substrate heating.
- SP-SiO $_2$:deposited with SP method at 200°C and then annealed in N $_2$ at 600°C for 2 hours.
- APCVD-SiO₂ :deposited with APCVD method at 350% and then annealed in N₂ at 600% for 2 hours.

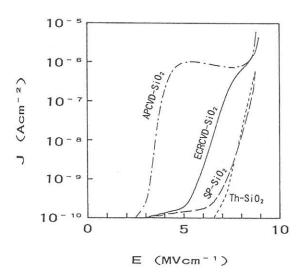


Fig.4 The J-E characteristics of MOS capacitors.

The J-E characteristics of $ECRCVD-SiO_2$ and SP-SiO₂ films were close to that of Th-SiO₂ in comparison with APCVD-SiO₂. However, the J-E curve of ECRCVD-SiO₂ had a small shoulder between 5 and 8 MV/cm.

The breakdown characteristics of ECRCVD-SiO₂ films were examined in detail as shown in Fig. 5. The breakdowns mainly occured at 9~10 MV/cm and a little of breakdowns at 2~7 MV/cm. These low field breakdowns and small shoulder in the J-E curve both indicated that $ECRCVD-SiO_2$ film had some weakspots caused by carrier traps.

The quasi-static C-V characteristics of the above-mentioned MOS capacitors are shown in Fig. 6. The characteristics of ECRCVD- SiO_2 films was very close to that of Th- SiO_2 .

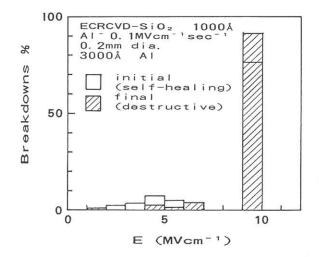


Fig.5 The breakdown distributions of MOS capacitors using $ECRCVD-SiO_2$ deposited without substrate heating.

Figure 7 shows the distributions of interface state density (Nss) calculated by using the quasi-static C-V characteristics. The interface state density between ECRCVD-SiO₂ films and c-Si was as low as that of Th-SiO₂ and 3.2×10¹⁰ (cm⁻² eV⁻¹) near the silicon mid-gap. The film of ECRCVD-SiO₂ deposited without substrate heating had an exellent interface properties which were comparable to those of Th-SiO₂. It seems to be due to rather low energy bombardment of ions to the substrate compared with the SP method.

As a result, it was proved that ECRCVD was a very hopeful method for high quality SiO_2 films deposition at low temperature below 600°.

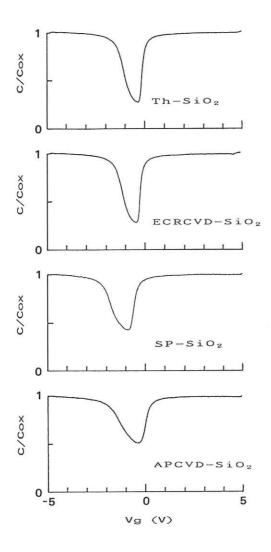


Fig.6 The quasi-static C-V characteristics of MOS capacitors.

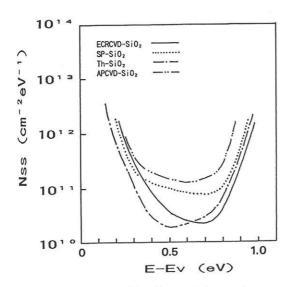


Fig.7 The distribution of interface state density of MOS capacitors,which is calculated by using the quasi-static C-V characteristics in Fig. 6.

4.SUMMARY

In order to develop the deposition method of high quality silicon oxide films at low temperature below 600°, ECRCVD, SP, APCVD methods were studied. Refractive index , etching rate and breakdown field of $ECRCVD-SiO_2$ film and $SP-SiO_2$ film were comparable to those of $Th-SiO_2$ film. The C-V characteristics of ECRCVD-SiO₂ film without substrate heating were very close to that of Th-SiO₂ film. Interface state density of ECRCVD-SiO₂ film was 3.2×10¹⁰ (cm⁻²eV⁻¹) near the silicon mid-gap. It was confirmed that ECR-CVD method was one of the most hopeful method for high quality SiO₂ film deposition at low temperature below 600°.

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REFERENCES

- S.Matsuo and M.Kiuchi: Jpn.J.Appl.Phys.
 22(1983) L210.
- T.Fukuda, K.Suzuki, S.Takahashi, Y.Mochizuki,
 M.Ohue and N.Momma: Jpn. J.Appl.Phys.<u>27</u>(1988)
 L1962.
- M.Kitagawa, T.Hirao, T.Ohmura and T.Izumi: Jpn.J.Appl.Phys.28(1989) L1048.
- T.Fukuda, M.Ohue, N.Momma, K.Suzuki and T.Sonobe: Jpn. J. Appl. Phys. 28(1989) 1035.
- 5) T.V.Herak, T.T.Chau, D.J.Thomson, S.R.Mejia, D.A.Buchaman and K.C.Kao: J.Appl.Phys. 65(1989) 2457.
- S.Suyama, A.Okamoto and T.Serikawa: IEEE Trans.Electron.Devices ED34(1987) 2124.
- T.Ohwaki and Y.Taga:Appl.Phys.Lett.
 28(1989) 837.
- J.Batey and E.Tierney: J.Appl.Phys.<u>60</u> (1986) 3136.
- 9) M.Kuhn:Solid-State Electron.13(1970) 873.