ELSEVIER

Journal of Non-Crystalline Solids 187 (1995) 81–85

JOURNAL OF NON-CRYSTALLINE SOLIDS

Effects of plasma treatment on the properties of room-temperature liquid-phase deposited (LPD) oxide films

Ching-Fa Yeh*, Shyue-Shyh Lin

Department of Electronics Engineering and Institute of Electronics, National Chiao-Tung University, Hsinchu, Taiwan

Abstract

Effects of plasma treatment including H_2 or O_2 on the properties of LPD oxide were investigated. After plasma treatment, the physicochemical characteristics of LPD oxide films were greatly improved. No matter whether with H_2 or O_2 plasma treatment, the LPD oxide film exhibited higher refractive index and lower P-etch rate than as-deposited films. The electrical characteristics were also improved. This indicates that plasma treatment can effectively passivate the vacancies in LPD oxide. It was also found that the treatment using O_2 source was better than using H_2. This was the same as for the case of thermal annealing. Because the plasma treated LPD oxide exhibited superior results to the thermally annealed one and the temperature in plasma treatment was much lower than that in thermal annealing, plasma treatment is more suitable for improving the characteristics of LPD oxide films.

1. Introduction

In recent years, much attention has been paid to liquid-phase deposited (LPD) silicon dioxide [1–6] for its extremely low-temperature processing and simple apparatus. The electrical properties of LPD oxide are better than those of chemical vapor deposited (CVD) oxide [3], but still worse than those of thermal oxide. In order to further enlarge the application of LPD oxide film to VLSI fabrication, much higher quality of LPD oxide and a better interface have to be achieved.

To improve the quality of the CVD oxide film, thermal annealing has usually been adopted [7–10]. In the previous study by Yoshitomi et al. [11], LPD oxide films after O_2 thermal annealing showed much improved characteristics. However, the annealing temperature had to be 600°C, which was so high that the merit of low-temperature LPD oxide would be lost. In this study, we have tried to use plasma treatment, which is low-temperature process, to improve the properties of LPD oxide.

2. Experimental

Experimental apparatus and basic equilibrium equations for LPD oxide deposition have been described in detail in our previous study [4]. Thus, we only give a brief description of the LPD process in this study.

The immersing solution was prepared with 75 g of silica added to 1.4 l of H_2SiF_6 solution at 23°C. After stirring and filtering out undissolved silica,

* Corresponding author. Tel: +886-35 712 121, ext. 3288 Telefax: +886-35 711 992.

0022-3093/95/$09.50
SSDI 0022-3093(95)00116-6

a solution saturated with silica was obtained. Then, the saturated solution was diluted to a concentration of 3.8 mol/l. In order to make a supersaturated state in the solution, a boric acid solution (0.1 mol/l) was added. When a Si substrate was immersed into the supersaturated solution, a deposition of oxide film started rapidly. All the samples were prepared at 30°C, while the film thickness was mainly controlled by immersion time.

The n-type (1 0 0) substrates with 4–7 Ω cm were used. After deposition, the samples were subject to H_2 or O_2 plasma treatment at 300°C for one hour. Plasma treatment was performed in a commercial 13.5 MHz parallel-plate plasma reactor with power density of 0.7 W/cm^2. A gas mixture of H_2/N_2 (60 sccm/60 sccm) at 0.25 torr was used in the H_2 plasma treatment and O_2 gas (150 sccm) at 0.25 torr was used in the O_2 plasma treatment. For comparison, some samples were treated by thermal annealing at 600°C in O_2 ambient.

The film thickness and refractive index were measured ellipsometrically. The P-etch rate was examined using the solution (48% HF : 70% HNO_3 : H_2O = 3 : 2 : 60 in volume) at room temperature. The chemical composition was analyzed by Auger electron spectroscopy (AES). The electrical characteristics of the LPD oxide film, such as leakage current, breakdown field and interface state density were evaluated with metal oxide semiconductor (MOS) capacitors. The area of the Al gate electrode was 0.126 mm^2.

3. Results and discussion

3.1. Physical/chemical effect

To understand the effects of plasma treatment on the physical/chemical properties of the films, we investigated the refractive index and P-etch rate first. The results for LPD oxide films with and without plasma treatment are summarized in Table 1. The results of the sample with 600°C O_2 thermal annealing are also shown for comparison. At first, we found that the refractive index of the LPD oxide after plasma treatment increased nearly to the value of thermal oxide. As reported in other studies, the oxide film with a lower refractive index had a less dense structure [12] and contained fluorine [13]. So, from the change of refractive index, we concluded that the LPD oxide structure was denser after plasma treatment. This conclusion was consistent with the results of the P-etch rate test, which indicated that the P-etch rate of LPD oxide decreased after plasma treatment. The denser the LPD oxide structure becomes, the lower the value of the P-etch rate. The reason why LPD oxide became denser after plasma treatment may also be due to the release of fluorine contained in the film. This fluorine-release effect could also increase the refractive index of LPD oxide [13]. Studies concerning the mechanism of release for Si–F bonds are still in progress.

Table 1
Summary of refractive index and P-etch rate of LPD oxide films with plasma treatment and thermal annealing

LPD oxide films	Refractive index, n	P-etch rate (Å/s)
As-deposited	1.43	20
H_2 plasma	1.45	9.2
O_2 plasma	1.456	7.5
600°C O_2 annealing	1.432	7.6

Comparing the difference between O_2 and H_2 plasma treatment in Table 1, we find that the refractive index of LPD oxide after O_2 plasma treatment had a higher value of refractive index and lower value of P-etch rate than those after H_2 plasma treatment. This was consistent with the results of thermal annealing [11]. To investigate this phenomena, the atomic composition for the LPD oxide with O_2 or H_2 plasma treatment was studied. Figs. 1(a)–(c) showed the result for as-deposited LPD oxide and LPD oxide after O_2 or H_2 plasma treatment, respectively. The AES depth profile indicated that O/Si ratio in the LPD oxide with O_2 plasma treatment was larger than that with H_2 plasma treatment. These results imply that the O_2 plasma diffused O_2 molecules into the film and filled the oxygen vacancies [14]. As a result the film became much denser in structure. Because the oxygen molecules were more suitable to fill the oxygen vacancies, the effect of the O_2 plasma treatment

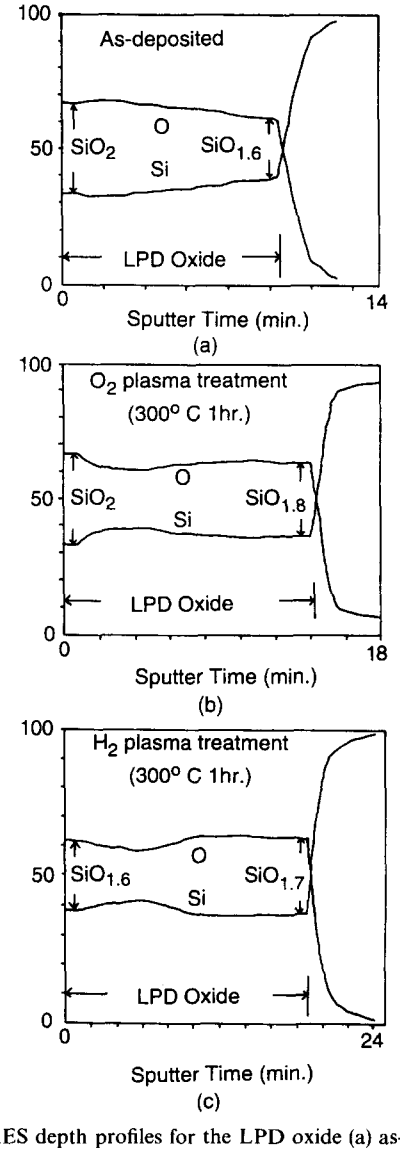

Fig. 1. AES depth profiles for the LPD oxide (a) as-deposited, (b) with O_2 plasma treatment, and (c) with H_2 plasma treatment.

was better than that of H_2 plasma treatment on improving the properties of LPD oxide.

As shown in Table 1, the effect of plasma treatment appears to be better than that of the thermal annealing for the refractive index and the P-etch rate. It implies that plasma treatment is a good procedure for replacing thermal annealing to improve the properties of LPD oxide.

3.2. Electrical effects

To further check the effect of plasma treatment on the properties of LPD oxide, the electrical characteristics of LPD oxide including I–V and interface-state were investigated. The typical I–V characteristics of LPD oxide films before and after plasma treatment for 1 h are shown in Fig. 2. The characteristics of the sample with O_2 thermal annealing are also shown for comparison. The plasma-treated samples showed a lower leakage current at low electric field (< 3 MV/cm) and a higher breakdown field than as-deposited and thermal annealed samples. In particular, the sample with the O_2 plasma showed a much higher breakdown field than that with H_2 plasma. This phenomenon was suspected to be due to less oxygen vacancies in the structure of O_2 plasma-treated LPD oxide. That is, the LPD oxide with O_2 plasma treatment had a denser structure and better atomic composition, and as a result exhibited better electrical characteristics. In comparison with O_2 thermal annealing (600°C), the results also reveal that the O_2 plasma treatment could effectively passivate the defects in LPD oxide film at low temperature. The histogram of breakdown field for the samples including as-deposited, O_2 annealed, H_2 plasma

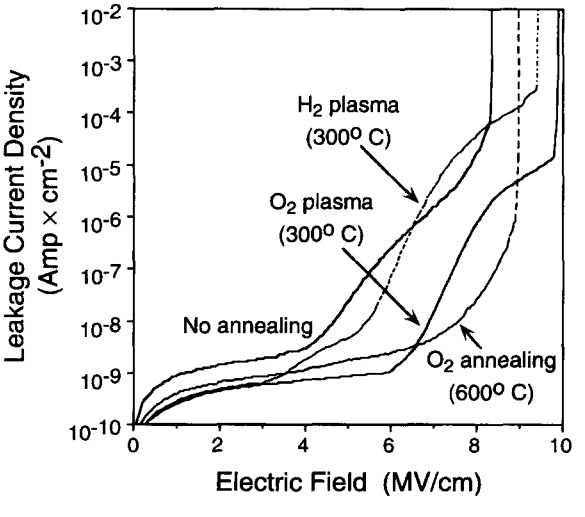

Fig. 2. J–E characteristics for the samples with and without plasma treatment and the sample with O_2 thermal annealing at 600°C.

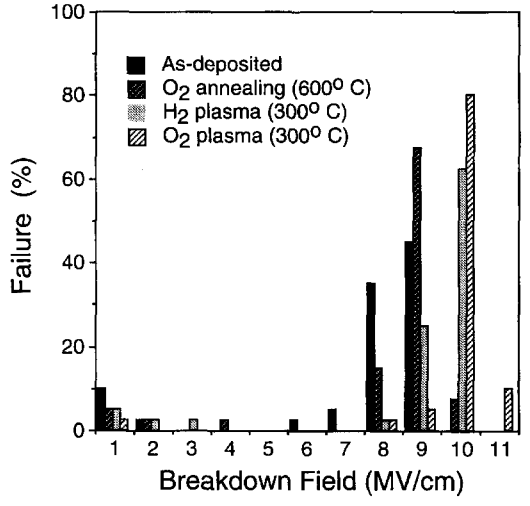

Fig. 3. Breakdown field histogram for the LPD oxide with or without plasma treatment and the sample with O_2 thermal annealing at 600°C.

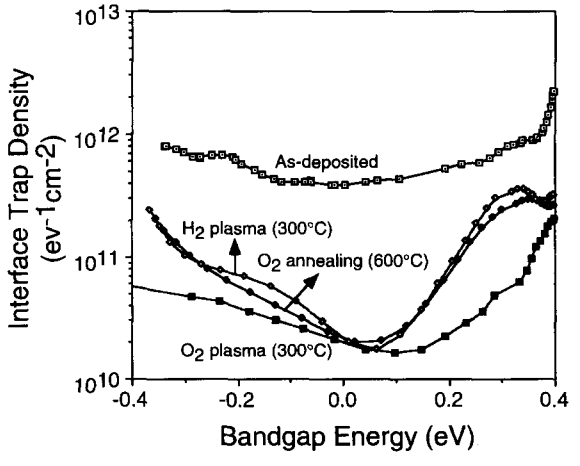

Fig. 4. Interface state density distribution for the samples with and without plasma treatment and the sample with O_2 thermal annealing at 600°C. Lines are drawn as guides for the eye.

and O_2 plasma are shown in Fig. 3. We find that the O_2 plasma-treated LPD oxide has a better distribution at high breakdown field than others.

To investigate the interface characteristics of LPD oxide after plasma treatment, the interface trap densities (D_{it}) for the samples after O_2 or H_2 plasma treatment were calculated by the Terman method [15]. As shown in Fig. 4, the interface trap density was about $5 \times 10^{11}\ eV^{-1}\ cm^{-2}$ for as-deposited samples, while it was as low as $2 \times 10^{10}\ eV^{-1}\ cm^{-2}$ for O_2 plasma treated samples. The improvement of D_{it} at midgap was almost the same for the samples with O_2 or H_2 plasma treatment, and it is suspected that H or O could passivate the interface traps at midgap [16]. In addition, the reduction of D_{it} at the band edge by O_2 plasma treatment was more obvious than that by H_2 plasma treatment. The interface traps near the band edge were attributed to be oxygen vacancies and weak Si–O bonds [17], so in O_2 plasma treatment oxygen might diffuse into the films and reduce D_{it} near the band edge.

4. Summary

The physicochemical characteristics of LPD oxide films after plasma treatment exhibit great improvement. They have higher refractive index and lower P-etch rates because they have denser structures and less fluorine. The electrical characteristics also exhibited much improvement: there is a lower leakage current and higher breakdown field due to the passivation effect. The plasma treatment using O_2 was more effective than using H_2. The plasma treatment also appeared superior to thermal annealing. Thus we conclude that plasma treatment is a more suitable method for improving the characteristics of LPD oxide films.

This work was supported by the National Science Council, Taiwan, under contract number NSC-83-0404-E-009-121.

References

[1] N. Nagayama, H. Honda and H. Kawahara, J. Electrochem. Soc. 135 (1988) 2013.
[2] T. Goda, H. Nagayama, A. Hishinuma and H. Kawahara, Mater. Res. Sym. Proc. 105 (1988) 283.
[3] C.F. Yeh, S.S. Lin, C.L. Chern and Y.C. Yang, IEEE Electron Device Lett. EDL-14 (1993) 403.
[4] C.F. Yeh, S.S. Lin, T.Z. Yang, C.L. Chern and Y.C. Yang, IEEE Trans. Electron Devices ED-41 (1994) 173.
[5] T. Horiuchi, K. Kanba, T. Homma, Y. Murao and K. Okumura, IEEE Trans. Electron Devices ED-40 (1993) 1455.

[6] T. Homma, T. Katoh, Y. Yamada and Y. Murao, J. Electrochem. Soc. 140 (1993) 2410.
[7] J. Lee, I.C. Chen and C. Hu, IEEE Electron Device Lett. EDL-7 (1986) 506.
[8] B.K. Ip, K.C. Kao and D.J. Thomson, Solid State Electron. 33 (1990) 123.
[9] M. Shyiang-Chyong Luo and C.T. Sah, Proc. Int. VLSI-TSA Conf. (1987).
[10] C.T. Sah, Solid State Electron. 33 (1990) 147.
[11] S. Yoshitomi, S. Tomioka and N. Haneji, Proc. 1992 Int. Electron Devices and Materials Symp. (1992) p. 22.
[12] W.A. Pliskin, J. Vac. Sci. Technol. 14 (1977) 1064.
[13] J.W. Fleming and D.L. Wood, Appl. Opt. 22 (1983) 3102.
[14] J. Perriere, B. Pelloie, E. Fogarassy and A. Slaoui, Appl. Surf. Sci. 29 (1987) 433.
[15] E.H. Nicollian and J.R. Brews, MOS (Metal Oxide Semiconductor) Physics and Technology (Wiley, New York, 1982).
[16] T. Sakurai and T. Sugano, J. Appl. Phys. 52 (1981) 2889.
[17] H. Fukuda, M. Yasuda and T. Iwabuchi, J. Appl. Phys. 72 (1992) 1906.