Highly Reliable Liquid-Phase Deposited SiO₂ with Nitrous Oxide Plasma Post-Treatment for Low Temperature Processed Poly-Si TFT's

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Abstract

Low temperature (~300°C) N_2O plasma annealing for liquidphase deposited (LPD) gate oxide has been proposed for the first time. Physicochemical and electrical characterizations show that the N_2O -treated LPD-SiO₂ improves breakdown field, interface state density, and Si-rich phenomenon. This novel technology has been also successfully applied to LTP poly-Si TFT's, which reveal excellent characteristics and reliability. It is believed that the N_2O plasma post-treatment not only improves the oxide quality, but also passivates the trap states in poly-Si channel.

Introduction

The development of high-quality gate oxide film is an important issue for fabricating low temperature processed (LTP) poly-Si TFT's. Recently, The way of liquid-phase deposited oxide (LPD-SiO₂) has been accepted much attention for the advantages of room temperature process (< 30°C), plasma-damage free and inexpensive apparatus [1-3], as compared with that using CVD and PVD techniques. In the past, we had successfully applied LPD-SiO₂ to LTP poly-Si TFT's as the gate insulator [4] and improved the oxide quality by way of furnace annealing in O_2 ambient [5]. According to that reported in [6-7], nitridation of oxide can further improve Si/SiO₂ interface properties and provide superior electrical characteristics and oxide reliability. In this paper, we will first apply the low temperature (~300°C) N₂O plasma annealing technology to the LPD oxide. Results of physicochemical and electrical properties will be then compared with that by furnace annealing. Also, the poly-Si TFT's with the N₂O-treated LPD gate oxide will be fabricated and evaluated. Finally, it will be pointed out that

Table 1 Basic characteristics for LPD-SiO $_2$ with different post-treatment conditions.

| Annealing Condition | thickness (Å) | refractive index | P-etch rate (Å/s) | dielectric constant 3.459 3.632 3.776 | |
|-----------------------------|------------------|---------------------|----------------------|---|--|
| As-deposited | 352 | 1.395 | 20.7 | | |
| Furnace(600°C O2 1hr) | 354 | 1,396 | 6.7 | | |
| N ₂ O Plasma 5' | 386 | 1.419 | 9.2 | | |
| N ₂ O Plasma 15' | 465 | 1.430 | 8.3 | 3.847 | |
| O ₂ Plasma 5' | 354 | 1.396 | 13.9 | 3.562 | |
| O, Plasma 15' | 352 | 1,396 | 14.2 | 3.542 | |



Fig. 1 AES depth profiles for N_2 O-plasma (5 min) post-treated LPD-SiO₂. the N_2 O plasma post-treatment is important and indispensable for improving TFT performance and reliability.

Experiments

A. Preparation of N_2O plasma post-treated LPD-SiO₂

The chemical reaction for LPD-SiO₂ growth can be simply represented by the following equilibrium reaction:

$$H_2 SiF_6 + 2H_2 O \leftrightarrow 6HF + SiO_2 \qquad \Delta H < 0. \tag{1}$$

The deposition rate of LPD-SiO₂ is controlled by change of H_2O quantity. First, Hydrofluorosilicic acid with saturated SiO₂ was prepared at 23°C for 17 hours and the Si substrates with native oxide were then immersed into the supersaturated solution at 18°C, where SiO₂ was deposited on the test samples by adding enough water. Finally, the LPD-SiO₂ samples were performed N₂O plasma treatment for 5-15 minutes.

B. Fabrication of LTP Poly-Si TFT's

Low temperature poly-Si TFT's are fabricated with a maximum processing temperature of 600° C. Undoped 1000Å-thick poly-Si film and 370Å-thick LTP-SiO₂ was deposited as the active layer and gate insulator, respectively. After deposition of the LPD gate oxide, the N₂O plasma was performed for 5-15 minutes to form the SiN_xO_{2-x} composition. The top-gate structures with self-aligned implantation were



Fig. 2 SIMS depth profiles for as-deposited LPD-SiO₂.



Fig. 3 SIMS depth profiles of LPD-SiO₂ after N_2O plasma post-treatment for 5 minutes.

adopted and 5000 Å-thick tetraethyl orthosilicate (TEOS) SiO_2 was deposited as the passivation layer. After contact holes were opened, a 5000 Å-thick aluminum layer was evaporated and patterned. Aluminum sintering was performed at 400°C for 30 minutes. The detailed fabrication procedures are described in the earlier report [8].

Results and Discussion

A. Physicochemical Characteristics of LPD-SiN_xO_{2-x}

Table 1 shows the basic characteristics of LPD-SiO₂ with O₂ and N₂O plasma post-treatments. The result of O₂ furnace annealing is also shown for comparison. After the N₂O plasma post-treatment, both refractive index and dielectric constant increase, which implies that the N₂O plasma reoxidizes LPD-SiO₂, and hence improves the oxide structure. The small p-etch rate also indicates the superior densification of LPD-SiN_xO_{2-x} film. Fig. 1 shows the AES depth profiles for the N₂O plasma post-treated LPD-SiO₂. The N₂O plasma improves the Si-rich phenomenon and reduces the fluorine concentration rather than the as-deposited LPD-SiO₂. In



Fig. 4 C-V characteristics of the LPD-SiO $_2$ with different post-treatment conditions.

addition, it is found that nitrogen atoms are piled up at Si/SiO_2 interfaces. The result can be further verified by the SIMS experiments. Fig. 2 and Fig. 3 show the SIMS depth profiles for the as-deposited LPD-SiO₂ and the LPD-SiN_xO_{2-x}, respectively, where the concentration of nitrogen in the as-deposited LPD-SiO₂ is extremely low, while a pronounced increase of nitrogen concentration in the LPD-SiN_xO_{2-x} is observed. From the above results, it can be noted that most of the nitrogen atoms in the LPD-SiN_xO_{2-x} pile up at the Si/LPD-SiO₂ interface, and some of them exist in oxide bulk.

B. Electrical Characteristics of LPD-SiN_xO_{2-x}

Fig. 4 shows the C-V characteristics of LPD-SiO₂ with different post-treatment conditions, where curves of the LPD-SiN_xO_{2-x} samples are shifted toward left side as compared with that of the as-deposited and O₂ plasma samples. It implies the breaking of Si-OH and Si-F bonds, so OH and F ions are diffused out from the LPD-SiO₂ film. These escaped



Fig. 5 Comparisons of interface trap densities for the LPD-SiO₂ with different post-treatment conditions.

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negative ions will subsequently leave oxygen vacancies $O_3 \equiv Si Si \equiv O_3$, which can be thought as the positive charges. and therefore results in the left shift of C-V curves. Fig. 5 shows the comparisons of interface trap densities (D_{it}) for the LPD-SiO₂ with different post-treatment conditions. The N₂O sample has smaller D_{it} (~10¹⁰ eV⁻¹cm⁻²) as compared with the as-deposited sample $(7 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2})$. It can be attributed to the excellent improvement of LPD oxide, which is due to the oxygen diffusion as well as the nitrogen incorporation into the Si/LPD-SiO₂ interface. The nitrogen incorporation forms a buffered layer, which is composed of Si=N bonds within the first 10Å from the interface and Si=N-O bonds outside of the first 10Å region [9]. The buffered layer plays an important role in reducing the interface stress, caused by the Si lattice-mismatch between the Si bulk and the oxide overlayer. The lattice-mismatch mainly results from the incomplete bonding of Si⁺² and Si⁺³. The J-E characteristics of the LPD-SiO₂ with different post-treatment conditions are shown in Fig. 6. At lower electrical field, the leakage current



Fig. 6 J-E characteristics of LPD-SiO₂ with different post-treatments.



Fig. 7 Weibull plots of breakdown field for LPD-SiO₂ with different post-treatments.



Fig. 8 Fowler-Nordheim plots of LPD-SiO2 with different post-treatments.



Fig. 9 Comparison of transfer characteristics for the LTP poly-Si TFT's with different post-treatment conditions.

density for all samples is nearly the same ($\sim 2 \times 10^{-9} \text{ A/cm}^2$). However, after the N₂O plasma post-treatment for 5 minutes, the electrical breakdown field of the LPD-SiO₂ is obviously higher (~11.0MV/cm) than that of other samples. In addition, the onset-tunneling field of the N₂O sample is also larger than that of others. They can be attributed to that the N₂O plasma treatment effectively relieves the interfacial stress and improves the Si-rich phenomenon. The strong Si-N bonds prevent electrons from direct tunneling between Si islands. Fig. 7 shows the Weibull plots of electrical breakdown field for different LPD samples. As described in Fig. 6, the N₂O sample has the largest electrical breakdown field and best breakdown uniformity than other samples. Fig. 8 shows the Fowler-Nordheim plots for different LPD samples, where a linear relationship for all samples is obtained. The barrier height at the Si/LPD-SiO₂ interface is calculated from these linear plots. As shown in Fig. 8, the LPD-SiN_xO_{2-x} improves barrier height of the as-deposited LPD-SiO₂ from 1.78 to 3.36eV.

C. Performance and Reliability for LTP poly-Si TFT's

Fig. 9 shows the transfer characteristics for the LTP poly-Si TFT's with different post-treated LPD gate oxide. It is clear that the N₂O sample much improves the electrical characteristics such as driving current, off-state current, subthreshold slope and threshold voltage rather than the furnace annealing and O₂ plasma samples. The calculated device parameters of all samples are summarized in Table 2. For the N_2O plasma sample (5 min), μ_{FE} increased from 7.71 to 16.31 cm²/Vsec and V_T decreased from 11.89 to 7.14 V. The superior device characteristics suggest that the N₂O sample has lower trap-state density and grain barrier height in the poly-Si channel. Fig. 10 shows the ON-current degradations as a function of stress time for different TFT samples under the stress of $V_{GS}=V_{DS}=15V$. The degradation of the N₂O sample is smaller than that of other samples. As it was known that the degradation of such an on-state stress is mainly due to the breaking of weak Si-Si and Si-H bonds, which generally forms the metastable trap states. The N2O plasma treatment can effectively passivate trap states and replace these weak Si-Si bonds with the strong Si-N bonds. Fig. 11 shows the ON-current degradation as a function of stress time for different TFT samples under the stress of $V_{DS}=0V$ and $V_{GS}=20V$. The N₂O sample reveals much better stress endurance than other samples. It implies that the N₂O sample can prevent electrons from trapping in the gate oxide. From the above results, the excellent gate-oxide reliability in N₂O sample can be thought as the incorporation of nitrogen atoms at the LPD-SiO₂/poly-Si interface, which forms strong Si-N bonds and hence relieves the interfacial stress.

Conclusion

In conclusion, a highly reliable LPD-SiN_xO_{2-x}, deposition of LPD-SiO₂ followed by N₂O plasma treatment, has been developed for low temperature and high quality gate oxide. From the analysis of physico-chemical and electrical properties, the LPD-SiN_xO_{2-x} reveals improved oxide quality and interface characteristics such as dielectric constant, Sirich phenomenon and interface trap density. As applied to LTP poly-Si TFT's, the device performance and reliability of the LPD-SiN_xO_{2-x} TFT are better than the furnace annealing and O₂ plasma TFT's.

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Table 2 Calculated device parameters for the LTP poly-Si TFT's with different post-treatment conditions.

| Gate Oxide Post-Annealing | V., (V) | Swing (V/dec) | Ι _{οΝ} (μΑ) | I _{o pr} (pA) | I _{on} ,I _{off} | μ_{FE} (cm ² /V·sec) | N, (cm ⁻²) |
|------------------------------|------------|------------------|-------------------------|---------------------------|-----------------------------------|--|---------------------------|
| Furnace | 11.89 | 1.708 | 37.06 | 45.70 | 8.11×10' | 7,71 | 1.29×10 ¹³ |
| N,O Plasma 5' | 7.14 | 1.250 | 194.6 | 59.05 | 3.30×10* | 16.31 | 7.55×10 ¹² |
| N ₂ O Plasma 15' | 7.57 | 1.398 | 132.1 | 113.8 | 1.16×10* | 13.92 | 6.62×10 ¹² |
| O ₁ Plasma 5' | 8.94 | 1.304 | 146.5 | 99.85 | 1.46×10* | 14.55 | 8.01×1012 |
| O, Plasma 15' | 8.93 | 1.285 | 148.4 | 56.10 | 2.65×10° | 14.80 | 8.10×10 ¹² |



Fig. 10 ON-current degradation with stress time for the LTP poly-Si TFT's with different post-treatment conditions under the stress of $V_{GS}=V_{DS}=15V$.



Fig. 11 ON-current degradation with stress time for the LTP poly-Si TFT's with different post-treatment conditions under the stress of V_{DS} =0V, V_{GS} =20V.

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