Superthin O/N/O Stacked Dielectrics Formed by Oxidizing Thin Nitrides in Low Pressure Oxygen for High-Density Memory Devices

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Abstract— **High-performance superthin oxide/nitride/oxide (O/N/O) stacked dielectrics have been successfully achieved by oxidizing thin nitride films in low-pressure dry-oxygen at 850 °C for 30 min. Since the nitrides exhibit a better oxidation resistance to the low-pressure dry-oxygen than to the atmospheric-pressure dry-oxygen and wet-oxygen, the low pressure oxidation obtains a thinner oxidized nitride for the high-density dynamic-random-access-memories (DRAM's) and metal-oxide-nitride-oxide-semiconductor (MONO'S) memory devices. In addition, this dielectric possesses low leakage current and excellent time-dependent-dielectric-breakdown (TDDB) characteristics. Therefore, this novel recipe is promising for future ULSI technology.**

FOR high-density DRAM and MONO'S memory devices, oxide/nitride (O/N) stacked dielectrics formed by atmospheric-pressure (AP) wet-oxidizing thin Si_3N_4 in a short duration have been extensively applied. As currently practiced, the Si_3N_4 cannot be reduced below 70 Å because it cannot withstand the wet-oxidation step [1]. This limits the implementation of the oxidized nitrides for the higher-density memory devices, even though this dielectric exhibits low defect density and the techniques are sophisticated for industry. Some recipes and new materials [2], [3] were studied to meet the requirements of further scale-down rules. However, many obstacles still exist to be conquered. In this study, a new technique of oxidizing thin Si_3N_4 in the low-pressure (LP) dry-oxygen is proposed to fabricate high-performance dielectric which possesses low leakage current, high reliability, and high capacitance for the memory devices.

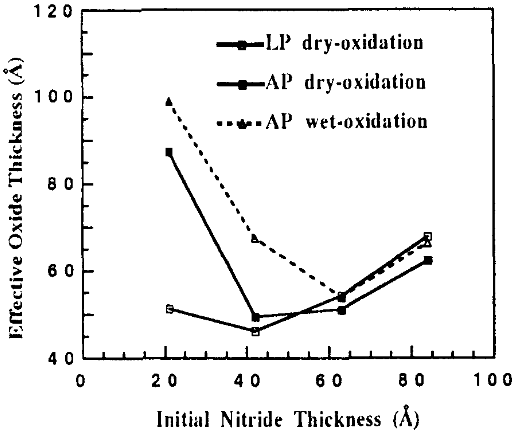

Fig. 1. The dependence of the effective oxide thickness of the dielectrics fabricated by oxidizing the nitride films with different oxidation schemes on the initial nitride thickness.

(100) oriented, 2.5-3.5 Ω-cm, both p-type and n-type Si wafers were used. After RCA cleaning, the LPCVD Si_3N_4 films were deposited at 750 °C for various times. The thicknesses of Si_3N_4 films ($t_{N,ini}$) were measured to be ranging from 23 Å to 84 Å by an ellipsometer using a constant refractive index of 2.0. Then, some specimens were atmospheric-pressure-dry-oxidized (760 Torr) and low-pressure-dry-oxidized (0.5 Torr) in pure O_2 ambient at 850 °C for 30 min. In addition, some wafers were also wet-oxidized in an atmospheric-pressure pyrogenic ambient at 850 °C for 5 min. After a 2500 Å-thick LPCVD poly-Si was deposited and subsequently $POCl_3$-diffused at 850 °C for 30 min, the MOS capacitors with various dielectrics were fabricated. To avoid the charge depletion effect, positive ($+Vg$) and negative ($-Vg$) gate-bias I-V measurements were conducted on n-type and p-type substrates, accordingly. The effective oxide thickness is determined by the high-frequency CV measurements and calculated by using a dielectric constant of 3.9 for the oxidized nitride films.

Fig. 1 shows the dependence of the effective oxide thickness ($t_{ox,eff}$) of the dielectric fabricated by oxidizing the Si_3N_4 with different oxidation schemes on the Si_3N_4 thickness. For all the samples with $t_{N,ini}$ above 60 Å, the Si_3N_4 films oxidized by different schemes exhibit the similar $t_{ox,eff}$. It reveals that the thick nitrides have similar oxidation resistance for all the oxidation methods. For the AP wet-oxidation, the $t_{N,ini}$ below 60 Å show fast oxidation and the lowest $t_{ox,eff}$ is 54 Å. As for the AP dry-oxidation, the dielectrics display fast growths only as the Si_3N_4 decreases to be as thin as 40 Å and the $t_{ox,eff}$ of 50 Å is obtained. In contrast, for the low-pressure oxidations, the Si_3N_4 still indicates a mild oxidation even as the Si_3N_4 to be lower than 40 Å and the minimum $t_{ox,eff}$ is 46 Å. Therefore, the low-pressure dry oxidation can

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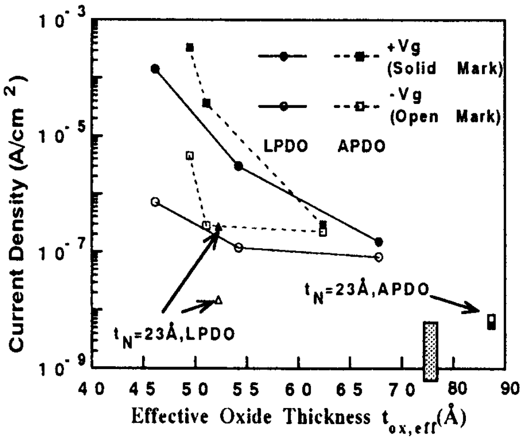

Fig. 2. The leakage current densities as a function of the effective oxide thickness ($t_{ox,eff}$) for the low-pressure-dry-oxidized (LPDO) and atmospheric-pressure-dry-oxidized (APDO) specimens. The samples were measured at $Vg = +3.3$ V for the n-type wafers and $Vg = -3.3$ V for the p-type wafers.

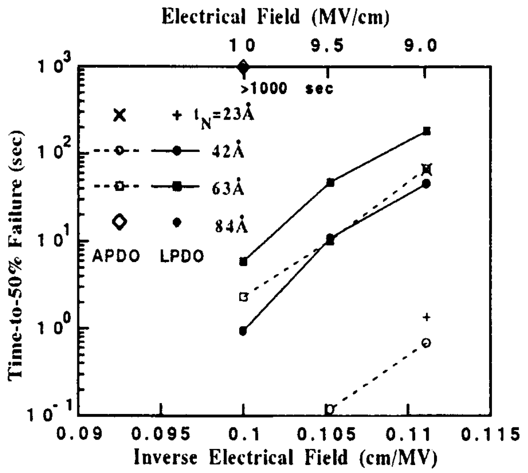

Fig. 3. The plots of time-to-50 % accumulated failure versus inverse electrical fields for various dielectrics after the constant voltage stressing from +9 MV/cm to +10 MV/cm at 100°C.

retard the fast growth of the oxidized nitrides as the $t_{N,ini}$ is thin and can obtain very low $t_{ox,eff}$.

Because the $t_{ox,eff}$ of the AP wet-oxidized Si_3N_4 cannot be further scaled down to be below 54 Å, this experiment puts efforts on the low-pressure-dry-oxidized (LPDO) and atmospheric-pressure-dry-oxidized (APDO) samples. Fig. 2 shows the leakage current densities as a function of the $t_{ox,eff}$ for the LPDO and APDO specimens, which the samples were measured at $Vg = +3.3$ V for the n-type wafers and $Vg = -3.3$ V for the p-type wafers. The current densities of the LPDO specimens is obviously lower than those of the APDO samples as the $t_{ox,eff}$ is below 60 Å. Particularly, the significant improvement in leakage current is observed for the LPDO samples as the $t_{ox,eff}$ is smaller than 50 Å. Exceptionally, the low leakage current of the samples with the $t_{N,ini}$ of 23 Å is measured, which is attributed to the significant oxidation of the nitrides, as shown in Fig. 1, and needed to be further studied. The TDDB characteristics were carried out by applying constant electrical field stressing ranging from +9 to +10 MV/cm at 100 °C. Fig. 3 shows the time-to-50 % accumulated failure as a function of inverse electrical fields for various dielectrics. All the defect density distributions of various dielectrics are comparable to the conventional oxidized nitrides, i.e., the AP wet-oxidized samples. For the dielectrics with $t_{N,ini}$ of 42 Å and 63 Å, the LPDO specimens also possess higher reliability than the APDO samples. In contrast, for the samples with the $t_{N,ini}$ of 23 Å, both the LPDO and APDO specimens undergo significant oxidation, and therefore express different TDDB characteristics.

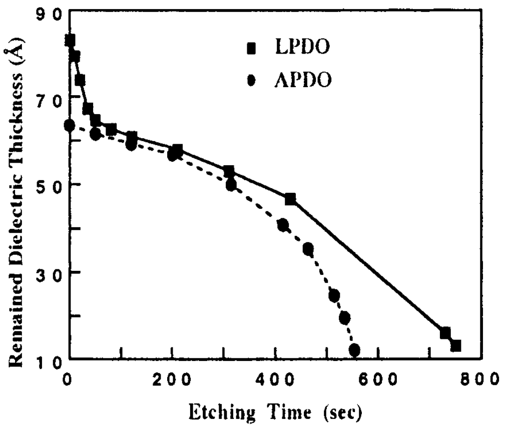

Fig. 4. The remained dielectric thickness as a function of the etching time for the AP and LP dry-oxidized nitrides with an initial nitride thickness of 63 Å after a step-by-step diluted-HF etching.

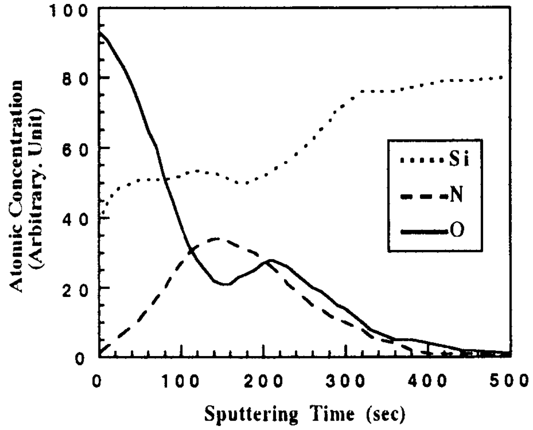

Fig. 5. The AES depth profile of the sample with a 63 Å-thick initial nitride after LP dry-oxidation.

To realize the compositions of the LPDO samples, a step-by-step diluted HF etching ($HF:H_2O = 1:100$) [4] were performed. Fig. 4 shows the remained dielectric thickness as a function of the etching time for the LPDO and APDO specimens with $t_{N,ini}$ of 63 Å. The remained thickness of the dielectrics is measured by the ellipsometer using a constant refractive index of 2.0. Three segments of etching rates were observed for the LPDO samples, but only two for the APDO samples. Because the etching rate of the Si_3N_4 is much slower than that of the SiO_2, it can be conjectured that an O/N/O structure is formed during the LPDO and a N/O structure for the APDO. The composition of each layer was further proved by the AES depth profile, as shown in Fig. 5, for the samples with $t_{N,ini}$ of 63 Å after the LPDO. It has been reported [5] that oxygen will diffuse through thin nitrides and therefore form the bottome oxides. Hence, the main difference is that top-oxide can be grown upon the thin nitrides for the LPDO but not for the APDO. Since the O/N/O structure has been reported to significantly lower the leakage current and increase the reliability [6], the distinct top-oxide is therefore surmised to be the main factor of improving the electrical characteristics for the LP dry-oxidation samples.

Due to the better oxidation resistance, the $t_{ox,eff}$ of the LP dry-oxidized Si_3N_4 can be further reduced. Furthermore, the dielectrics possess the low leakage current and high reliability because of top-oxide growth. Therefore, this novel technique to form superthin O/N/O dielectric is promising for the high-density memory devices.

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