Application of Anodization to Reoxidize Silicon Nitride Film

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Anodic reoxidation of ultrathin Si_3N_4 film in deionized (DI) water followed by rapid thermal annealing (RTA) in N_2 (ANO) was for the first time studied in this work. The Si_3N_4 film directly reoxidized in O_2 by RTA (O_2RTA) was used for comparison. It was found that the reoxidation process could significantly improve the characteristics of chemical-vapor-deposited (CVD) Si_3N_4 in terms of both the interface and bulk qualities. The ANO samples show lower leakage current, lower interface trap and bulk trap densities, and higher breakdown field than O_2RTA of the same equivalent oxide thickness (EOT). The better electrical characteristics of ANO are due to more oxygen atoms incorporated into the Si_3N_4 films during the anodic reoxidation.

KEYWORDS: anodization, anodic reoxidation, nitride, XPS

1. Introduction

As the scaling of silicon complementary metal-oxide semiconductor (CMOS) devices shrinks further into the sub-micron range, thermally grown SiO_2 with a thickness below 2 nm must be used as the gate dielectric to meet the high-performance requirement for the devices. The direct tunneling current becomes an important factor for limiting the reduction of oxide thickness.¹⁾ Alternative insulator materials with a dielectric constant k greater than 3.9 are therefore considered due to their increased physical thickness under the same capacitance with the thinner SiO_2 .

In finding alternative dielectric materials, silicon nitride films, such as oxynitride,^{2,3)} reoxidized nitride,⁴⁾ and jet-vapor-deposited (JVD) nitride films,^{5–7)} have been extensively studied because of their higher permittivity ($k = 7.2$) and more effective suppression of Boron penetration⁸⁾ into the substrate than silicon oxide films. However, thick silicon nitride films are known to have a high leakage current density, which is strongly related to its poor nitride film quality, *e.g.*, too many charge traps and high interface state density.⁹⁾ However, in the ultrathin region (direct tunneling region), Si_3N_4 film shows a markedly reduced number of charge trapping and enhanced detrapping of trapped charges due to tunneling,¹⁰⁾ both of which contribute to reduced leakage current and improved hot-carrier reliability. Furthermore, reoxidation of Si_3N_4 films has been reported to reduce the electron trap density as well as suppress the interface-state generation under electrical stress.¹¹⁾ It is noted that thin bottom oxides between Si_3N_4 and Si can be formed during reoxidation of Si_3N_4 .¹²⁾ However, the thickness of the bottom oxides that might limit the scaling of the effective dielectric thickness and degrade the time-dependent dielectric breakdown characteristic must be considered.^{13,14)} Many research studies were focused on the dominant charge carrier flow inside the nitride or oxidized nitride dielectrics, and it was found that electrons and holes are the dominant conduction carriers in the oxide and nitride, respectively.¹⁵⁾ It was also reported that when oxide was grown on the nitride, the hole flow through the nitride can be blocked by the oxide and hence the total gate leakage current is reduced.⁴⁾

In this work, we present a novel method of reoxidizing

the Si_3N_4 film. Room-temperature anodic reoxidation in deionized (DI) water was used to reoxidize Si_3N_4 for the first time. According to existing literature,^{16,17)} anodic oxides exhibit excellent electrical characteristics such as low leakage current, high dielectric breakdown field, and high effective electron barrier height. With the additional merits of low thermal budget and low cost, anodic oxidation is attractive in high-density integrated circuit application. It was found that Si_3N_4 films prepared by anodic reoxidation show much-improved characteristics than the original chemical-vapor-deposited (CVD) Si_3N_4 . Also, they are better than the thermally reoxidized ones.

2. Experiment

To evaluate the effects of different reoxidation processes on Si_3N_4 , both anodic reoxidation and conventional thermal reoxidation were used in this study. Six-inch p-type Si wafers were used. After standard RCA cleaning with final HF dip, ultrathin Si_3N_4 films of 2.5 nm thickness were formed with SiH_2Cl_2 and NH_3 at 700°C by low-pressure chemical vapor deposition (LPCVD).

In the ANO procedure, the wafer with the Si_3N_4 film acts as an anode. A constant electrolyzing voltage of 20 V was applied for 10 and 15 min separately at room temperature using DI water as an electrolyte. The schematic diagram of the anodic oxidation system is shown in Fig. 1. After the anodization procedure, post-anodic-oxidation rapid thermal annealing at 950°C for 30 s in N_2 ambient was performed to induce hydrogen evolution from the oxidized nitride films. In rapid thermal annealing (RTA) in O_2 , *i.e.*, O_2RTA , a conventional RTA system was utilized to oxidize the Si_3N_4 films at 900°C and 950°C for 20 s in O_2 ambient separately. In order to determine the atom distribution, the surface bonding condition and the atomic concentration, all the samples were examined by high-resolution secondary ion mass spectrometer (SIMS; Cameca, IMS-4f) and X-ray photoelectron spectroscopy (XPS; Physical Electronics, ESCA PHI 1600).

After the Si_3N_4 reoxidation processes, aluminum of about 2000 Å thickness was thermally evaporated on the front side surface and followed by photolithography to define the gate electrode. Then, backsurface metallization was implemented for the back contact of metal-oxidized nitride-Si capacitors. In addition, metal-oxide-Si (MOS) capacitors with thermal

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Fig. 1. Schematic diagram of anodic reoxidation system.

oxide layers of 2 nm thickness as the gate dielectric were also fabricated at the same time for comparison. Standard capacitance–voltage (C – V) and current–voltage (I – V) measurements were used to investigate the electrical properties of the devices. Also, the equivalent oxide thickness (EOT) was obtained from high-frequency (100 KHz) C – V measurements in strong accumulation region using a dielectric constant of 3.9, considering the quantum mechanism effect.

3. Results and Discussion

3.1 Depth profile analysis

Results of SIMS analysis of samples after different reoxidation processes of Si_3N_4 films are shown in Fig. 2. In this figure, it is observed that no matter which reoxidation process was employed, very thin oxide buffer layers appear on the top and around the dielectric/silicon interface as shown by the accumulation of oxygen atoms. These interfacial buffer oxides can effectively improve the quality of the nitride interface by reducing the interface trap density.¹⁸⁾ In addition, the hole flow through the nitride faces a large barrier height due to the presence of interfacial oxide.¹⁵⁾ The distributions of Si–N

Fig. 2. SIMS depth profile of Si–N and O counts for Si_3N_4 samples after RTA reoxidation in O_2 ambient (O_2RTA) and ANO. Cs^+ is used as sputtering ion in this analysis.

and O atoms in the bulk and the surface are different between anodic reoxidation (ANO) and O_2RTA samples. We can observe that more oxygen atoms were incorporated into the films after anodic reoxidation. It is known that Frankel–Pool (F–P) emission is the main conduction mechanism of Si_3N_4 . Traps play an important role in the migration of carriers through the films. Also, the reoxidation of Si_3N_4 films has been proposed to eliminate the electron traps.¹¹⁾ It is therefore believed that these unwanted bindings or defects could be compensated during the reoxidation process, and more oxygen atoms incorporated in the films by anodic reoxidation could lead to the reduction in trap density and leakage current.

3.2 Surface bonding analysis

The surface bonding conditions after reoxidation of Si_3N_4 films were characterized by *ex situ* XPS using monochromatic Mg $K\alpha$ radiation. Many research studies^{10,19)} indicated that the N 1s with a peak energy of 397.99 eV is mainly related to the formation of $\text{N}\equiv\text{Si}_3$ bonds and that of 398.6 eV is $\text{N}=\text{Si}_2$. In the latter, each N atom is bonded to only two Si atoms with the remaining bond being a dangling bond. From these research studies, we found that in the presence of unwanted dangling bonds between the S–N networks on the surface, the N 1s peak energy position shifts to a higher energy level on the XPS spectra. Figure 3 shows the N 1s spectra of the original CVD nitride and two reoxidized samples. In this figure, the original Si_3N_4 peak energy position is located at 398.6 eV, indicating that a great amount of dangling bonds exist on the CVD nitride surface. It is observed that the peaks shift to a lower binding energy level after the reoxidation procedure. The binding energies are located at 397.7 eV and 398.4 eV for ANO and O_2RTA reoxidation, respectively. They are very close to those described above. From the spectra, we can observe that ANO reoxidation can convert the Si_3N_4 films to be more stoichiometric than O_2RTA reoxidation. It is believed that this formation of denser films is helpful in suppressing the boron penetration and reducing the boron-penetration-induced low field leakage current.¹⁰⁾ The XPS data were analyzed by means of a standard software package to calculate the atomic concentration. Si_3N_4 film not subjected to reoxidation was also taken into account in order to eliminate the

Fig. 3. Normalized N 1s XPS spectra of Si_3N_4 films after anodic reoxidation (solid line) and O_2 RTA reoxidation (dash line).

Fig. 4. Surface relative atomic concentrations (O, Si and N) in Si_3N_4 films after O_2RTA and ANO.

native oxide effect. As presented in Fig. 4, the concentration of the oxygen atoms in the ANO reoxidized sample (21.82%) is obviously higher than that in the O_2RTA sample (13.42%) on the surface. It is confirmed that more oxygen atoms can be incorporated into the Si_3N_4 film by anodic reoxidation, and the traps and defects in the bulk oxide can be repaired during reoxidation.

3.3 Characteristics of interface quality and leakage current

Figures 5(a) and 5(b) show high-frequency $C-V$ curves of silicon nitride reoxidized by ANO and O_2RTA , respectively. For the sample Si_3N_4 not subjected to any reoxidation treatment as shown in Fig. 5(c), its hysteresis loop is apparent, which may be attributed to the presence of electron traps in the interface. However, the hysteresis phenomenon becomes indistinguishable in the $C-V$ curves after the reoxidation treatment. We consider that both thermal and anodic

Fig. 5. $C-V$ characteristics of CVD Si_3N_4 (a) after anodic reoxidation 15 min, (b) after O_2 RTA reoxidation at 950°C , and (c) without any post-deposition treatment.

Fig. 6. $J-V$ characteristics of SiO_2 , CVD Si_3N_4 , $\text{Si}_3\text{N}_4 + \text{O}_2\text{RTA}$, and $\text{Si}_3\text{N}_4 + \text{ANO}$ samples.

reoxidation processes can improve the interface quality by reducing the electron traps and interface state density since thin oxide buffer layers can be grown in the interface.

As the oxide thickness is reduced below 2.0 nm in the next generation, the rapid increase of direct tunneling current becomes a major obstacle for the scaling. Figure 6 shows the comparison of gate injection tunneling currents through the dielectrics of 2.0-nm-thick oxide layer and the nitride films after reoxidation processes of ANO and O_2RTA under the same equivalent oxide thickness (EOT) of 2.0 nm. It is noted that the EOT value is defined by comparing the accumulation capacitance with that of the SiO_2 sample. In addition, the original 2.5-nm-thick CVD Si_3N_4 not subjected to reoxidation is also shown. From the current density-voltage ($J-V$) curves, it is apparent that reoxidation can significantly improve the CVD Si_3N_4 quality by reducing the leakage current. It is also noted that the gate currents of Si_3N_4 films after reoxidation are about 2–3 order of magnitude lower than that of the conventional SiO_2 at a bias of -1 V, which can be attributed to their greater physical thickness than the oxide under the same EOT. Furthermore, the ANO-reoxidized sample shows a leakage current of an order of magnitude lower than that of the O_2RTA sample. It is believed that the ANO oxide grown on the surface of the Si_3N_4 exhibits a more uniform electrical characteristic due to the self-compensation nature of the current path during anodization. A more uniform oxide exhibits less local thinning and therefore smaller leakage current. Meanwhile, ANO oxide with abundant oxygen atoms may reduce defect density in the bulk and therefore reduce the leakage current.

Figure 7 shows the comparison of time-zero-dielectric-breakdown (TZDB) characteristics of SiO_2 , ANO and O_2RTA samples with EOT of 2.0 nm. Compared with the conventional SiO_2 , the reoxidized Si_3N_4 films show a higher E_{bd} of 24–26 MV/cm with EOT of 2.0 nm. In addition, the ANO sample can suffer about ~ 1 MV/cm more than the O_2RTA sample before breakdown. It is believed that the reduction of electron traps in the ANO sample makes the breakdown via the electron-trapping mechanism difficult.

It is known that the trapping of positive charges under a constant current stress will result in a reduction in gate voltage, while that of negative charges an increase in gate voltage,

Fig. 7. Weibull plot of equivalent breakdown field for SiO_2 , $\text{Si}_3\text{N}_4 + \text{O}_2\text{RTA}$, and $\text{Si}_3\text{N}_4 + \text{ANO}$ samples.

Fig. 8. Variations of $\Delta V_g / |V_g|$ versus stress time under a constant current density of -10 mA/cm^2 for Si_3N_4 , $\text{Si}_3\text{N}_4 + \text{O}_2\text{RTA}$, and $\text{Si}_3\text{N}_4 + \text{ANO}$ samples.

age.²⁰ Figure 8 shows the variation of V_g under a -10 A/cm^2 current density stress. It shows a different trapping mechanism in that the original Si_3N_4 film contains a great amount of hole traps with respect to the reoxidized Si_3N_4 films. The latter exhibit net electron traps. We can note that the ANO sample presents a slightly more shift under stress. This is because the anodic reoxidation was performed in the liquid state. More OH^- ion related to the chemical species can be incorporated into the films than thermally grown oxide. It was reported that the dangling bonds in the silicon nitride are passivated by hydrogen.²¹ Also, it is known that the chemical species of $-\text{NH}_x$, $-\text{OH}$, and $-\text{H}$ act as electron traps in the oxide.²² A trade-off must be considered by controlling the hydrogen concentration in reoxidized Si_3N_4 to compensate for the hole traps in Si_3N_4 . However, the hydrogen problem is not serious for the ANO sample as compared with that of the O_2RTA one.

4. Conclusions

Characteristics of reoxidized Si_3N_4 by anodization were for the first time studied in this work. Reoxidation could obvi-

ously improve the Si_3N_4 quality including reduced interface trap and bulk trap densities based on the results of $C-V$ and $I-V$ measurements. It was found that the anodic reoxidation has the merits of lower leakage current, lower interface state density, and higher breakdown field compared with thermal reoxidation. It was shown that O atoms are easier to be incorporated into the Si_3N_4 film by anodic reoxidation. In addition, we can observe that $-\text{H}$ related to chemical species of the film might cause electron traps in the dielectric, which compensate the hole traps in the Si_3N_4 film. The anodic reoxidation appears to be an efficient method of preparing high-quality ultrathin reoxidized high- k dielectrics.

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