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Quality Improvement in LPCVD Silicon Nitrides by Anodic and Rapid Thermal Oxidations

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Low-pressure chemical vapor deposition (LPCVD) Si_3N_4 quality presents a dramatic improvement after oxidation. Both liquid-phase anodic oxidation and rapid thermal oxidation were studied in this work. After oxidation, “ SiO_2 ”-like layers grown on the surface, and oxygen incorporated into the Si_3N_4 layer were observed. The nonstoichiometric bonding, i.e., $\text{Si}_2=\text{N}$, Si dangling bonds, and crystalline Si were oxidized into $\text{Si}_2=\text{N}-\text{O}$ or SiO_2 , and the stoichiometric $\text{Si}_3\equiv\text{N}$ bonding maintained a higher- k property. In addition, more oxygen replacement of the imperfect Si-N bonds after anodic oxidation contributed to better improvement in suppressing gate leakage current.

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For the shrinkage of metal-oxide-semiconductor field-effect transistors (MOSFETs), device-grade ultrathin SiO_2 is necessary to meet the integrated circuit requirement. However, the increasing problems with boron penetration through ultrathin oxide and exponentially increased direct tunneling (DT) current dictate the replacement of the prospective dielectrics.¹ Alternative material with higher permittivity is therefore considered because of the greater physical thickness under the same capacitance. Among these high- k materials, silicon-based Si_3N_4 has been studied extensively, because of its high permittivity ($k = 6-8$, depends on stoichiometry), high processes compatibility, and good capability for suppressing boron penetration.² To obtain a stoichiometric Si_3N_4 film, the nitride-related technologies such as chemical vapor deposition (CVD) nitride,³ jet-vapor-deposited (JVD) nitride,⁴ atomic-layer-deposition (ALD),⁵ and nitrided- SiO_2 , i.e., oxynitride,⁶ have been studied extensively.

At the same time, Si_3N_4 grown by low-pressure chemical vapor deposition (LPCVD) is used to mask the active region or store the memory charges. CVD nitride exhibits a high throughput merit in batch processes. However, interactions of SiCl_2H_2 and NH_3 tend to form silicon-rich nitride films, a great amount of traps and unbounded dangling bonds are present. Also, the extended crystalline silicon would induce extra leaky gate current that is unfavorable for transistor gate insulator. From a previous report, oxidation of CVD nitride is significant in enhancing dielectric quality.⁷ Reaction between oxidant and CVD nitride plays a major role to compensate the imperfect bonding and reduce the traps. In addition, due to the barrier height difference under migration, electrons and holes were reported to be the dominant conduction carriers in SiO_2 and Si_3N_4 , respectively.⁸ When oxide is grown on the surface or incorporated into the nitride, the hole-flow current may be suppressed by the oxide, because the holes face a much higher barrier of SiO_2 ($\Phi_{\text{Bh}} = 4.4 \text{ eV}$) than Si_3N_4 ($\Phi_{\text{Bh}} = 1.8 \text{ eV}$).⁹ Accordingly, the total gate leakage current would be quenched after oxidation.

From our studies, anodic oxidation exhibits the merits of low thermal budget and better thickness uniformity than thermal oxidation.¹⁰ In this work, liquid-phase anodic oxidation and rapid thermal oxidation (RTO) were applied to oxidize CVD nitride films. CVD nitride presents a dramatic improvement in nitride quality after oxidation. Different oxygen incorporation regimes of thermal-enhanced and field-enhanced oxidations were observed. The ultimate nitride characteristics were affected by the varied oxidation processes.

Experimental

After standard RCA clean, ultrathin Si_3N_4 films of 20–30 Å were deposited on p-type silicon substrate by LPCVD with SiH_2Cl_2 and NH_3 at 700°C. Afterward, the nitride films were treated with either anodic oxidation or RTO. For the anodized samples, constant field of 10 V/cm was applied using deionized (DI) water as electrolyte. After anodic oxidation, postoxidation-annealing (POA) was performed to remove hydrogen from the films at 850°C 20 s in N_2 ambient. For rapid thermal oxidized samples, a conventional RTO system was utilized to oxidize the Si_3N_4 films at 850°C 20 s in O_2 ambient. After the silicon nitride films were oxidized by either anodic oxidation or rapid thermal oxidation, standard lithography and etching processes were used to define a metal-insulator-semiconductor (MIS) structure with an aluminum gate electrode.

Nitride depth profiles and atomic concentration distributions were examined by a high-resolution secondary-ion mass spectrometer (SIMS, Cameca, IMS-4f) and X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 250), respectively. Besides, the electrical properties were characterized by capacitance-voltage (C-V) and current-voltage (I-V) measurements. Considering the series resistance and quantum mechanical effects, equivalent oxide thicknesses (EOTs) were obtained from high-frequency C-V measurements in strong accumulation region.^{11,12}

Results and Discussion

During oxidation, oxidant diffuses toward the underneath silicon and the interaction may take place both in the bulk nitride and the silicon. To observe depth profile variation of Si and N before and after oxidations, SIMS with primary ions of Cs^{2+} (10 kv, 2 nA) was used to sputter the LPCVD nitride film. Profiles of Si and N are shown in Fig. 1a and b, respectively. In Fig. 1a, the plot shows Si profiles of as-grown CVD and those after rapid thermal and anodic oxidations. The stable and constant tails can be referred to as the silicon substrate region. For this reference point, we can observe the CVD nitride layer thickness increased after either rapid thermal or anodic oxidations. This result may imply two contributions: (i) Si is excess in the CVD Si_3N_4 network, hence SiO_2 is generated and (ii) interfacial SiO_2 is grown after oxidation. In addition, N profiles under the same process conditions are shown in Fig. 1b, the N counts were observed to be reduced after oxidation, especially after anodic oxidation. It is suspected that the oxygen could replace the unstable Si-N bonding under subsequent oxidation, and the excess nitrogen was then carried by the gas or the electrolyte during oxidation. Unlike Fowler-Nordheim (F-N) tunneling in SiO_2 , the major conduction mechanism of Si_3N_4 is known to be Poole-Frankel (P-F) emission. Traps from nonstoichiometric nitride bulk play an important role in the charge migration. Hence, it is believed that if the unbound Si or Si-N bonds were compensated by oxygen, the trap density may be effectively reduced. More oxygen incorporated in

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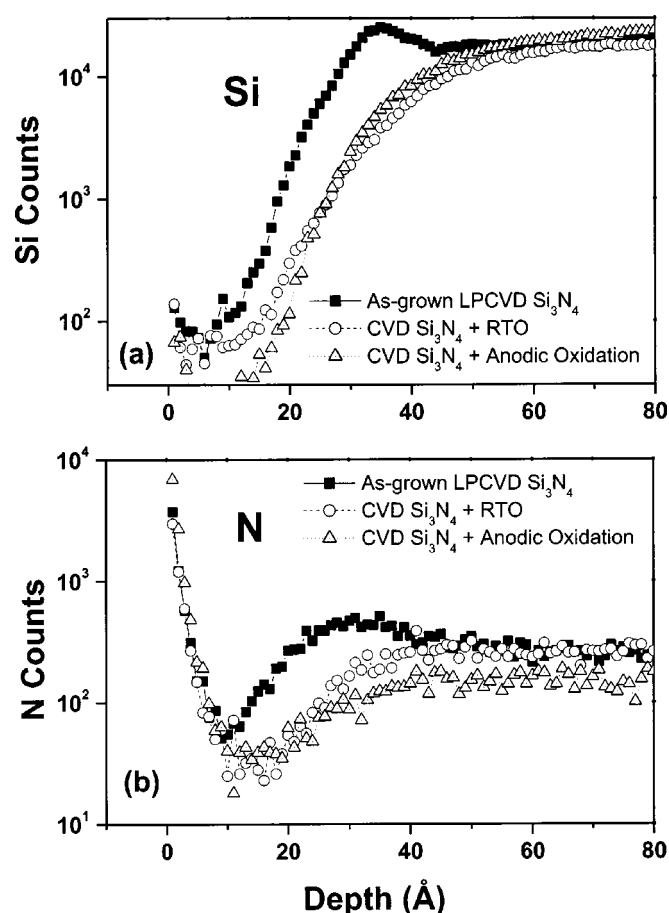


Figure 1. SIMS depth profiles of as-grown LPCVD Si_3N_4 , CVD Si_3N_4 after rapid thermal oxidation (RTO), and CVD Si_3N_4 after anodic oxidation. Profiles of Si and N are shown in (a) and (b), respectively.

the anodic Si_3N_4 reveals more replacements of unstable Si-N bonding by Si-O, which is helpful in reducing trap-assisted tunneling probability.

For advance understanding of the oxygen incorporation effects, XPS with a low and constant sputter rate (ionized Ar at 3 kV, $0.7 \mu\text{A}/\text{mm}^2$) is used to detect the depth profiles in atomic concentration. The profiles of as-grown Si_3N_4 (step 1-20), with rapid thermal oxidation (step 1-35) and with anodic oxidation (step 1-35) are shown in Fig. 2a, b, and c, respectively. It is obvious that Si_3N_4 grown by LPCVD tends to form silicon-rich film and the native oxide is easily grown such that O concentration, *i.e.*, [O] is even higher than N concentration, *i.e.*, [N] at the near-surface region. After oxidation, the total layer thickness increases as shown in Fig. 2b and c. “ SiO_2 ”-like layers were grown on the nitride surface after both oxidation processes. In addition, a nearly stoichiometric SiO_2 ($\text{Si}:\text{O} = 1:2$) layer was grown on the anodic Si_3N_4 surface. Because XPS resolution is not good enough to observe the interfacial thin layer condition, however, the clues can be obtained from the [O] distribution close to the substrate. In Fig. 2c, [O] presents a relatively higher value than in Fig. 2b, which implies more incorporated oxygen in the bulk and in the interface.

Figure 3 exhibits the XPS Si 2p spectra of the samples (as shown in Fig. 2a-c) at the surface region. It is known that Si 2p binding energies of 99.3, 102.2, and 103.3 eV correspond to Si, Si_3N_4 , and SiO_2 , respectively. Signals between them mainly accounted for the varied Si, N, and O bonding assembling or intermediate oxidation states, *i.e.*, suboxide or dangling bonds. Due to the thinner layer thickness, as-grown CVD nitride shows a stronger Si intensity from the substrate, and the other peak between 102.2 and 103.3 eV re-

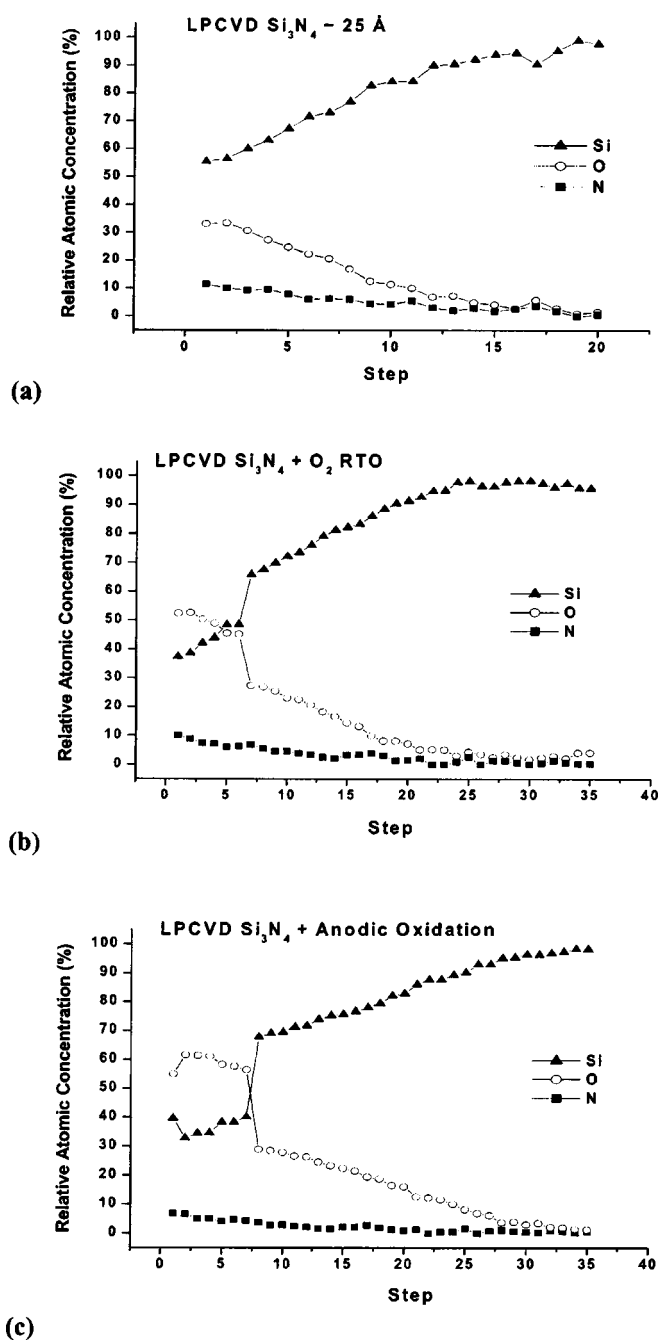


Figure 2. XPS depth profiles of [Si], [N], and [O] relative atomic concentration of (a) as-grown LPCVD Si_3N_4 , (b) LPCVD Si_3N_4 after rapid thermal oxidation, and (c) LPCVD Si_3N_4 after anodic oxidation.

veals the bonding of nitrogen and the native oxide. Also, it is obvious that the signal among the two peaks shows relative higher intensity than the other two curves. That reveals the great number of imperfect bonds before oxidation. By observing the curves after rapid thermal and anodic oxidations, Si from the substrate shows nearly the same signal intensity revealing a similar layer thickness. However, the higher SiO_2 signal intensity shows a more perfect surface oxide bonding after anodic oxidation. Also, from the analysis of N 1s on the surface (not shown), the peak position of rapid thermal oxidized N and anodic N were 398.3 and 397.8 eV, respectively, which were close to $\text{N}=\text{Si}_2$ (398.6 eV) and $\text{N}\equiv\text{Si}_3$ (397.99 eV).¹³ This implies that the more stoichiometric $\text{N}\equiv\text{Si}_3$ bonding

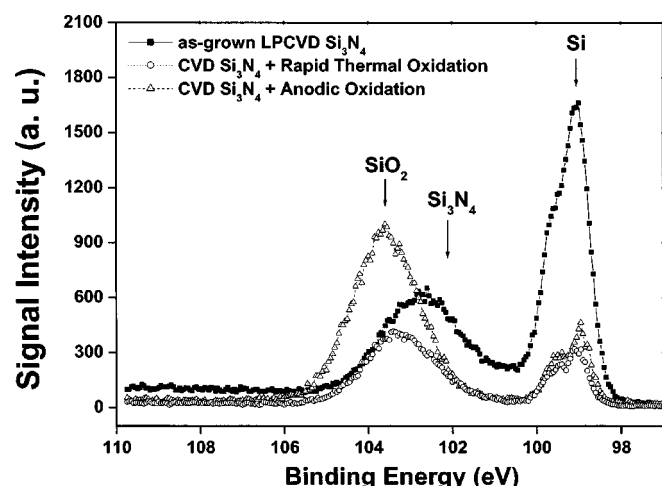


Figure 3. XPS Si 2p spectra of as-grown LPCVD Si_3N_4 , LPCVD Si_3N_4 after rapid thermal oxidation, and LPCVD Si_3N_4 after anodic oxidation which were detected on the sample surface.

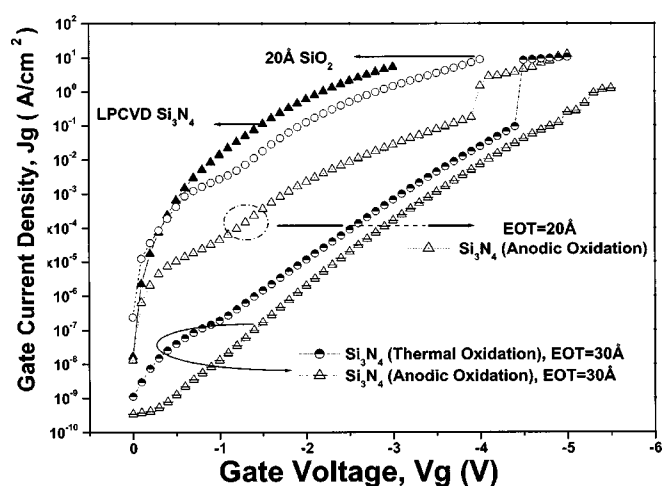


Figure 4. J - V comparison of conventional SiO_2 , as-grown CVD Si_3N_4 , and CVD Si_3N_4 treated with rapid thermal and anodic oxidations with different EOTs.

dominates the Si-N bonds network in the anodic nitride and more dangling bonds exist in the thermal oxidized nitride.

We believe that imperfect bonding, *i.e.*, unstable Si-N, Si dangling bonds, and crystalline Si may be oxidized into $\text{Si}_2 = \text{N}-\text{O}$ or SiO_2 , and stoichiometric Si_3N_4 bonding is not affected during oxidation. When thermal oxidation is utilized, high kinetic O mass irregularly reacts with the nonstoichiometric bonding and therefore produces a partial compensation. However under field-enhanced anodization, layer-by-layer interaction of OH^- and CVD nitride results in more complete compensation of the nonstoichiometric bonding. Therefore, a smoother and higher ratio of oxygen is observed to be incorporated in the anodic oxidized Si_3N_4 layer.

Gate leakage current comparison is shown in Fig. 4. Postoxidation presents a dramatic improvement in the CVD nitride property. Moreover, a “ Si_3N_4 ”-like layer may maintain a high- k property that is almost two orders of magnitude lower leakage current than SiO_2 under $\text{EOT} = 20 \text{ \AA}$ is observed. For rapid thermal and anodic oxidation treated nitrides with $\text{EOT} = 30 \text{ \AA}$, the anodic Si_3N_4 with more oxygen incorporated exhibits a lower gate leakage current. From previous results, the lower leakage current may be attributed to fewer imperfect bonds after anodic oxidation.

Conclusions

Postoxidation plays a critical role in improving CVD nitride quality. The O atom is easier to incorporate into Si_3N_4 film and replace the nonstoichiometric Si-N bonds by anodic oxidation. The reduced imperfect bonds are helpful in decreasing trap-assisted tunneling current. Therefore, if one can control the oxidation condition well, Si_3N_4 may be a promising high- k dielectric for advanced process utilization.

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References

1. B. Yu, H. Wang, C. Riccobene, Q. Xiang, and M. R. Lin, in *Proceedings of the Symposium on VLSI Technology*, p. 90 (2000).
2. Y. Wu and G. Lucovsky, in *IEEE 36th Annual International Reliability Physics Symposium*, p. 70 (1998).
3. F. H. P. M. Habraken and A. E. T. Kuiper, *Mater. Sci. Eng., R.*, **12**, 123 (1994).
4. Y. C. Yeo, Q. Lu, W. C. Lee, T. J. King, C. Hu, X. Wang, X. Guo, and T. P. Ma, *IEEE Electron Device Lett.*, **21**, 540 (2000).
5. H. Goto, K. Shibahara, and S. Yokoyama, *Appl. Phys. Lett.*, **68**, 3257 (1996).
6. C. Gerardi, M. Melanotte, S. Lombardo, S. Lombardo, M. Alessandri, B. Crivelli, and R. Zonca, *J. Appl. Phys.*, **87**, 498 (2000).
7. S. C. Song, H. F. Luan, C. H. Lee, A. Y. Mao, S. J. Lee, J. Gelpey, S. Marcus, and D. L. Kwong, in *Proceedings of the Symposium on VLSI Technology*, p. 137 (1999).
8. M. Aminzadeh, S. Nozaki, and R. V. Giridhar, *IEEE Trans. Electron Devices*, **35**, 459 (1988).
9. M. K. Mazumder, K. Kobayashi, J. I. Mitsuhashi, and H. Koyama, *IEEE Trans. Electron Devices*, **41**, 2417 (1994).
10. M. J. Jeng and J. G. Hwu, *Appl. Phys. Lett.*, **69**, 3875 (1996).
11. K. J. Yang and C. Hu, *IEEE Trans. Electron Devices*, **46**, 1500 (1999).
12. K. Yang, Y.-C. King, and C. Hu, *Technical Digest VLSI Symposium*, p. 77 (1999).
13. R. I. Hegde, P. J. Tobin, K. G. Reid, B. M. Maiti, and S. A. Ajuria, *Appl. Phys. Lett.*, **66**, 2882 (1995).