



Change in Depth Profile of N Highly Incorporated into SiO₂ by Plasma-Assisted Nitridation

M.-H. Cho,^{a,z} K. B. Chung,^a Y. K. Kim,^a D. C. Kim,^b J.-H. Heo,^b B. Y. Koo,^b
Y. K. Shin,^b U. I. Chung,^b J. T. Moon,^b and D.-H. Ko^c

^aNano Surface Group, Korea Research Institute of Standards and Science, Daejeon 305-600, Korea

^bSamsung Electronics Company Limited, Process Development Team, Semiconductor Research and Development Center, Yongin-City, Gyeonggi-Do 449-711, Korea

^cDepartment of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea

The depth profile in nitrided SiO₂ films using N₂ remote radio frequency plasma was investigated. N was incorporated into the film at levels of up to 27 atom %, largely concentrated at the film surface, and not the film interface. The depth profiling data showed that the depth of incorporated N is dependant on film thickness, i.e., N is incorporated to a depth of about 1.1 nm in a 1.5 nm thick film, while the depth is significantly less to about 0.7 nm in the case of a 4.0 nm thick film. Moreover, under the same nitridation condition, more N content is concentrated nearer to the surface of a 1.5 nm thick oxide film than that of 4.0 nm thick film. N₂, generated in the molecule during the nitrogen process is almost completely concentrated at the film interface. After an additional annealing treatment, the molecular N₂ diffuses out extensively and N, which is chemically bonded to Si₃, is changed into a more stable state with different second-nearest neighbors, accompanied by reoxidation at the film interface of an ultrathin film.

© 2006 The Electrochemical Society. [DOI: 10.1149/1.2184487] All rights reserved.

Manuscript submitted November 9, 2005; revised manuscript received January 26, 2006. Available electronically March 9, 2006.

Issues concerning the reliability of ultrathin gate dielectrics have become one of the most serious challenges in the scaling of ultralarge scale integration (ULSI) devices. In particular, the negative bias temperature instability (NBTI) in p-metal oxide semiconductor field effect transistors (p-MOSFETs) has become increasingly serious in terms of realizing highly reliable integrated complementary metal-oxide-semiconductor (CMOS) devices.¹ Moreover, attempts to scale the thickness of SiO₂ to below 2 nm have clearly demonstrated the limitations of SiO₂ in terms of high gate leakage current and poor resistance to boron penetration.² Nitrided silicon dioxide has been used to replace conventional SiO₂ as the dielectric of choice for gate dielectric applications of CMOS devices. However, the incorporation of nitrogen into gate oxides could significantly enhance NBT degradation.³ In order to prevent enhanced NBT degradation by nitrogen incorporation, it has been recently proposed that nitrogen atoms should be introduced near to the SiO₂ surface by plasma nitridation.⁴ It has been reported that the method used in plasma nitridation permits relatively large amounts of nitrogen to be incorporated into the film, which could effectively decrease NBT degradation and B penetration, and also provide good control over the nitrogen depth profile in the gate dielectric.^{5,6} Recent research has concentrated on clarifying the effect of nitrogen incorporation on reliability in MOSFETs using plasma nitridation. Some studies have also reported that the dependence of the process on nitridation influences intrinsic oxidation and the chemical bonding state at the interface between the oxynitride and Si after the reoxidation process.^{7,8} These reports only focus the effect of modification on ultrathin oxynitride films and its influence on device performance. More detailed depth profiling data for N concentration and changes in its chemical characteristics as a function of the depth profile of N have not been provided yet, although the physical characteristics significantly influence the improvement of reliability as well as modification of the oxide film after the postnitridation anneal (PNA).

We investigated the depth profile for the N content in nitrided SiO₂ film by plasma nitridation. N is incorporated at high levels into the film, up to 27 atom %, and is largely concentrated at the film surface, not the film interface. The N content in 4.0 nm thick film is effectively locally concentrated on the film surface, compared to that of a 1.5 nm thick film, i.e., in an ultrathin based oxide film below 1.5 nm, some portion of the N is incorporated into the film interface. Moreover, the amount of N incorporated into a film is dependant on

the thickness of the base SiO₂ film thickness, i.e., under the same nitridation conditions, a higher N content is incorporated into a 1.5 nm thick oxide film than that of 4.0 nm thick film. Molecular N₂ is generated during the nitridation process and is largely concentrated at the film interface, although the incorporated N accumulates locally on the film surface. After an additional annealing treatment in an ambient of inert nitrogen as a PNA, the molecule N₂ at the film interface nearly completely diffuses out, while the N that is chemically bonded to Si₃ is changed into a more stable state with different second-nearest neighbors. Reoxidation occurs at the film surface during the PNA, and it is extended to the interfacial area in an ultrathin 1.5 nm thick SiON film.

SiO₂ layers were grown at 400°C using a plasma oxidation process on p-type Si(001) wafers cleaned by the standard RCA cleaning method. A mixture of Ar/O₂ gas as a medium for plasma was introduced through the discharge cavity under a microwave power of 100 W. The film layer showed superior gate dielectric properties such as a reduced transition layer and high charge-to-breakdown to thermally grown SiO₂.⁹ The nitridation process was performed using an N₂ remote plasma (inductively coupled plasma 13.56 MHz) at an rf power of 700 W and the substrate temperature of 400°C. The N₂ flow rate was set by a mass flow controller at 60 sccm and the process pressure was fixed at 500 mTorr. In order to analyze the depth profile of N and chemical state of N in the depth direction as a function of film thickness, the base SiO₂ film thickness was controlled to 1.5, 2.5, and 4.0 nm. The depth profiling data and chemical state of the films were examined by synchrotron radiation X-ray photoemission spectroscopy (SRXPS) and medium energy ion scattering (MEIS) spectroscopy. An XPS experiment was carried out using synchrotron radiation at the Pohang Accelerator Laboratory, Korea. The incident photon energy was controlled from 440 to 1200 eV, and the energy resolution was about 0.1 eV at an incident photon energy of below 650 eV. The binding energy was calibrated with reference to the position of bulk Si 2p_{3/2} levels at *E_b* = 99.2 eV for each photon energy. Gaussian-Lorentzian line shapes were used for deconvolution after standard Shirley background subtraction. The binding energies of the three interface-shifted peaks are assigned as the suboxide states of Si atoms usually labeled S1 (Si¹⁺), S2 (Si²⁺), and S3 (Si³⁺) with the bulk Si peak labeled S0 (Si⁰) and the bulk oxide peak labeled S4 (Si⁴⁺).¹⁰

MEIS is a very sensitive technique for characterizing the depth profile of the chemical composition in ultrathin films. During the MEIS analysis, a 100 keV proton beam was aligned along the [001] direction and the protons scattered from the nitrided SiO₂ were analyzed under glancing angle conditions. The angular resolution and

^z E-mail: mhcho@kriss.re.kr

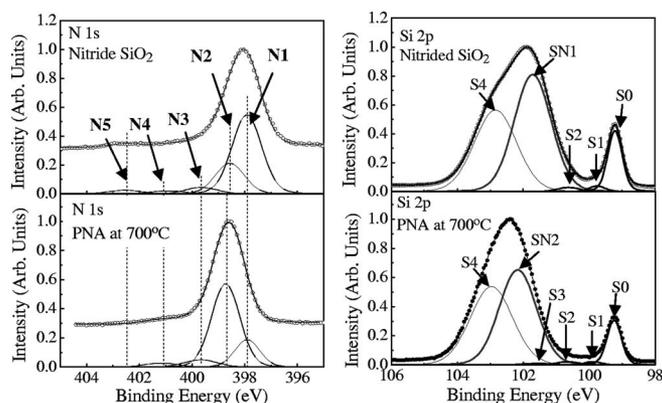


Figure 1. XPS spectra of N 1s (left side) and Si 2p (right side) in a nitrated SiO_2 thin film (1.5 nm). The bottom side shows the XPS data of Si 2p and N 1s after an additional anneal at 700°C as a PNA step. The lower Si $2p_{1/2}$ spin-orbit component was stripped and the background subtracted.

energy resolution of the MEIS were 0.1° and 0.003, respectively. Dielectric constant and electronic structure as a function of N content were investigated by capacitance-voltage (C-V) and near-edge X-ray absorption fine structure (NEXAFS) measurements, respectively.

Figure 1 shows the changes in binding energies for (a) N 1s and (b) Si 2p as SiON peaks measured by XPS on ultrathin plasma-nitrated (~ 1.5 nm) SiO_2 film and its postnitrated film. Reported data have shown that both the N 1s and Si 2p peaks shift to lower binding energies when the effective amount of N in the SiO_2 film is increased by varying the plasma conditions, indicating that a higher N concentration yields more $\text{Si}\equiv\text{N}$ bonds.¹¹ In all samples investigated, two main peaks in several N 1s peaks were observed for the peaks positioned at ~ 397.9 (N1) and 398.6 eV (N2). Comparing these peak with those of an additionally annealed sample, the deconvolution can be more clearly understood. From the N binding energy, the main peak at ~ 397.9 eV can be attributed to N atoms to which three Si atoms are bound in the planar structure, $\text{N}\equiv\text{Si}$.¹² Although the chemical state N2 is indistinguishable from N1, it can be related to N species with three Si nearest neighbors. The N2 species is different from N1 only with respect to the second-nearest neighbors, i.e., N2 corresponds to nitrogen atoms dispersed within the SiO_2 matrix, while N1 corresponds to those incorporated into the Si interfacial layers.¹² Minor peaks for N3 and N4 can be attributed to nonstoichiometric silicon oxynitride and $\text{O}_2=\text{N}-\text{Si}$ because the binding energy of the N 1s peak for SiN_x species shifts their binding energy to a much higher level, depending on x and nitrogen atoms that are bound to oxygen atoms.^{13,14} In our sample, the amount of N atoms after an additional PNA was found to be almost the same as that of as-nitrated film and the portion of N1 and N2 is clearly changed after the PNA. Thus, the peak changes in Si 2p and N 1s after an additional PNA at 700°C clearly indicate that the nitride state has changed to a more stable $\text{Si}\equiv\text{N}$ state. One interesting finding is that a chemical state with very high binding energy at 402.8 eV (N5), which is not chemically bonded to Si or O, is generated in the SiO_2 film during the nitridation process. In an investigated sample, more than one Si 2p peak related to SiON is observed, considering the peak symmetry and width of the nitrated SiO_2 film. The peak corresponding to the chemically bonded Si to N in the samples before and after PNA was roughly deconvoluted by two peaks positioned at 101.7 (SN1) and 103.1 eV (SN2), respectively, which reflects the relations to the N species with the three Si nearest neighbors, i.e., the SN1 peak position is almost the same as that for Si^{+3} (S3) caused by Si_3N_4 and SN2 peak shifts to higher position than the SN1 peak.

In order to characterize the chemical state and depth profile of N3, NEXAFS and XPS were measured, as shown in Fig. 2. The N

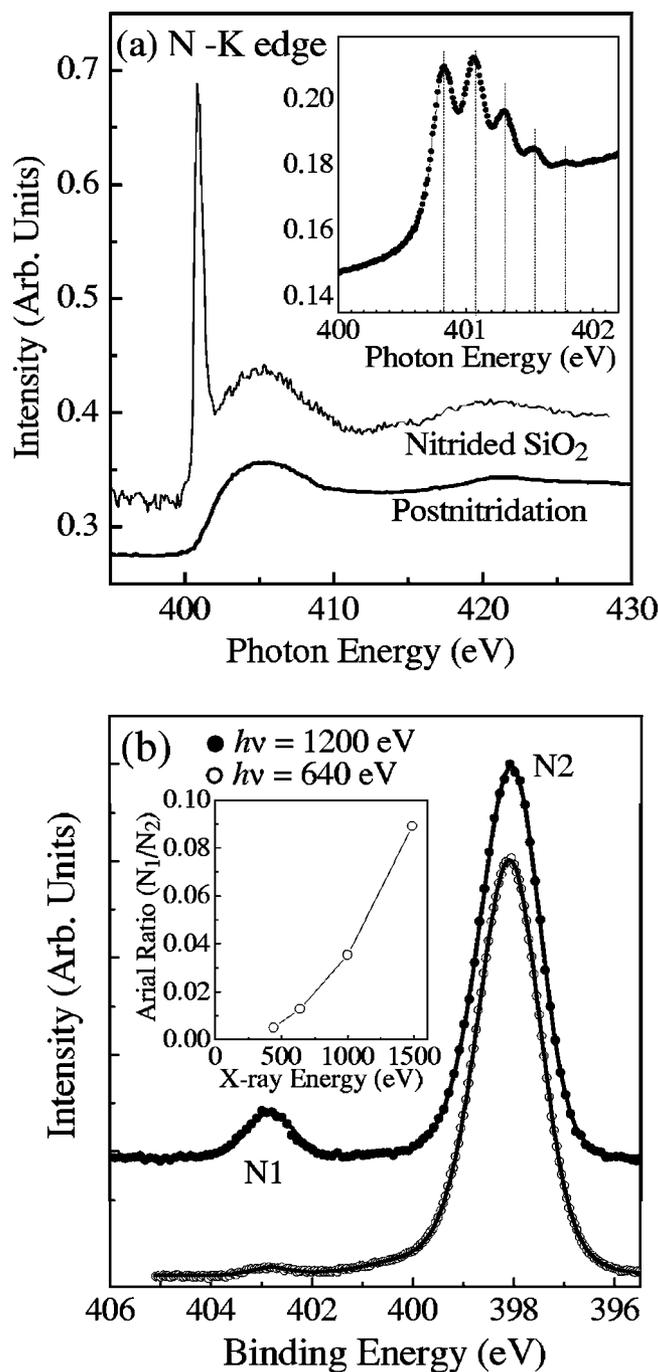


Figure 2. (a) N K-edge NEXAFS spectra of as-nitrated and annealed films. (b) N 1s XPS spectra of as-nitrated film depending on X-ray incident energy. The inset shows the ratio of the areas of N1 to N2 as a function of X-ray incident energy.

K-edge absorption spectrum exhibits a very sharp peak at 401 eV and a broad peak at 405 eV. The broad peak can be assigned to nitrogen bonded to Si and O, which is typically observed in nitrides and oxynitrides.¹⁵ The sharp peak can be caused by atomic N and molecular N_2 since their absorption peak is located at 401 eV with a sharp peak shape. A close inspection of the sharp peak at high resolution can lead to the conclusion that some discrete peaks are included at the 401 eV peak as shown in the inset of Fig. 1a, i.e., five well-resolved fine structures are observed. The fine structures are consistent with those of free N_2 molecules, which have been assigned to a transition from N 1s to the π^* orbital.¹⁶ Therefore, the

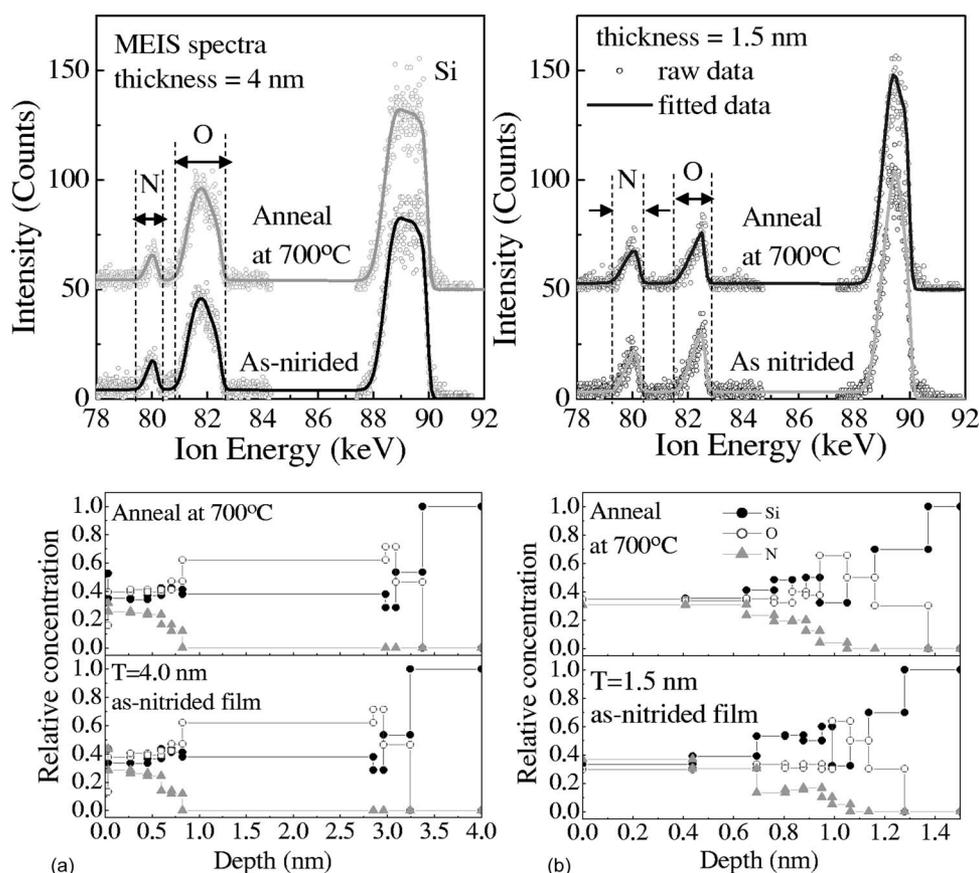


Figure 3. MEIS spectra of (a) 4.0 and (b) 1.5 nm thick as-nitrided and additional annealed films. The bottom part shows depth profiling data obtained from fitted MEIS spectra.

fine structure indicates that N_2 molecules are generated in the SiON films. The peak caused by N_2 state disappears after the postnitridation anneal, in agreement with the XPS result in Fig. 1. Comparing the NEXAFS and XPS data, we can conclude that the highest binding energy at 403 eV in XPS can be attributed to molecular N_2 . Another interesting finding is that the XPS peak height caused by molecular N_2 is dependent on incident X-ray energies, as shown in Fig. 2b. This dependency indicates that the molecular N_2 state is locally concentrated at the interfacial region. The angle resolved data also supports the localization of N_2 (data not shown here). In fact, the high density N_2 plasma employed in this study produces mostly energetic N_2 species such as N_2 radicals and N_2^+ ions in addition to atomic nitrogen species. Thus, the presence of energetic N_2 species impinging on the SiO_2 layer can be N_2 molecules that are formed at the interfacial region.¹⁴

The change in stoichiometry and the concentration of N in the depth profile of films with different thickness was investigated by means of MEIS. Figure 3 shows MEIS spectra of SiON films, prepared using different thicknesses and a postnitridation anneal. It is clear that the peak width and height, indicating the depth profile of N, differ substantially with film thickness. In a 1.5 nm thick SiON film, the depth of N incorporated is deeper than that of a 4.0 nm thick film, i.e., 0.7 nm for 4.0 nm thick film, while the value is 1.1 nm for the 1.5 nm thick film. Moreover, the total quantity of N incorporated into the 1.5 nm thick film (23.5 atom %) is larger than that for the 4.0 nm thick film (9.01 atom %). Based on the fine depth profile in the MEIS spectra at the film surface, the maximum surface concentration of N in a 1.5 nm thick film is higher than that of a 4.0 nm thick film, i.e., $[N]/[O] = 1.43$ for 1.5 nm thick film and $[N]/[O] = 0.76$ for 4.0 nm thick film. This result indicates that the amount of N incorporated into the SiO_2 film is significantly affected by the thickness of the base oxide. N is more easily incorporated into silicon-rich oxide than stoichiometric SiO_2 , since N replaces O

atoms to form Si—N bonds. Another possibility is that subcutaneous nitridation of the Si substrate occurs in the case of the thinner oxide. Therefore, a large portion of the interfacial region with a silicon-rich oxide layer in an ultrathin SiO_2 film is attributed to the higher incorporation of N in thin film than that for a relatively thick film.^{7,10}

After an additional annealing treatment at 700°C as a PNA, the quantity of incorporated N was not decreased. The XPS data in Fig. 1 after the additional PNA show that a portion of the Si≡N bonds was relatively decreased, while that of unstoichiometric silicon oxynitride was increased, compared to the nitride samples. Moreover, the peak change in Si 2p indicates that the film was reoxidized during the postnitridation anneal because the Si peak caused by the nitride film shifts to a higher binding energy.^{7,8} This effect is reflected in the MEIS depth profile, in which the quantity of O at the film surface is increased. In particular, at the interfacial region in a 1.5 nm thick film, it was slightly increased. Therefore, the change from the Si≡N bond to the unstoichiometric oxynitride during the postnitridation anneal accompanies the reoxidation of the film surface. In the case of an ultrathin film, the effect was extended to the interfacial region.

Finally, we investigated the C-V characteristics and calculated the dielectric constant from the accumulated capacitance from C-V data. Although the decrease in film thickness is considered, the accumulation capacitance is significantly increased when the thickness of the nitride film decreased, because the quantity of incorporated N is dependent on the film thickness, as shown in MEIS spectra. The calculated dielectric constant from the accumulation capacitance value is 5.7 and 5.1 for film thicknesses of 2.5 and 4.0 nm, respectively. The hysteresis loop change is negligible, indicating a small amount of trapped charge. For a film thickness of 2.5 nm, the dielectric constant can be controlled from 4.8 to 5.7 by the quantity of N content in the film. This change in dielectric constant clearly indicates a linear dependence on N content as shown in Fig. 4b,

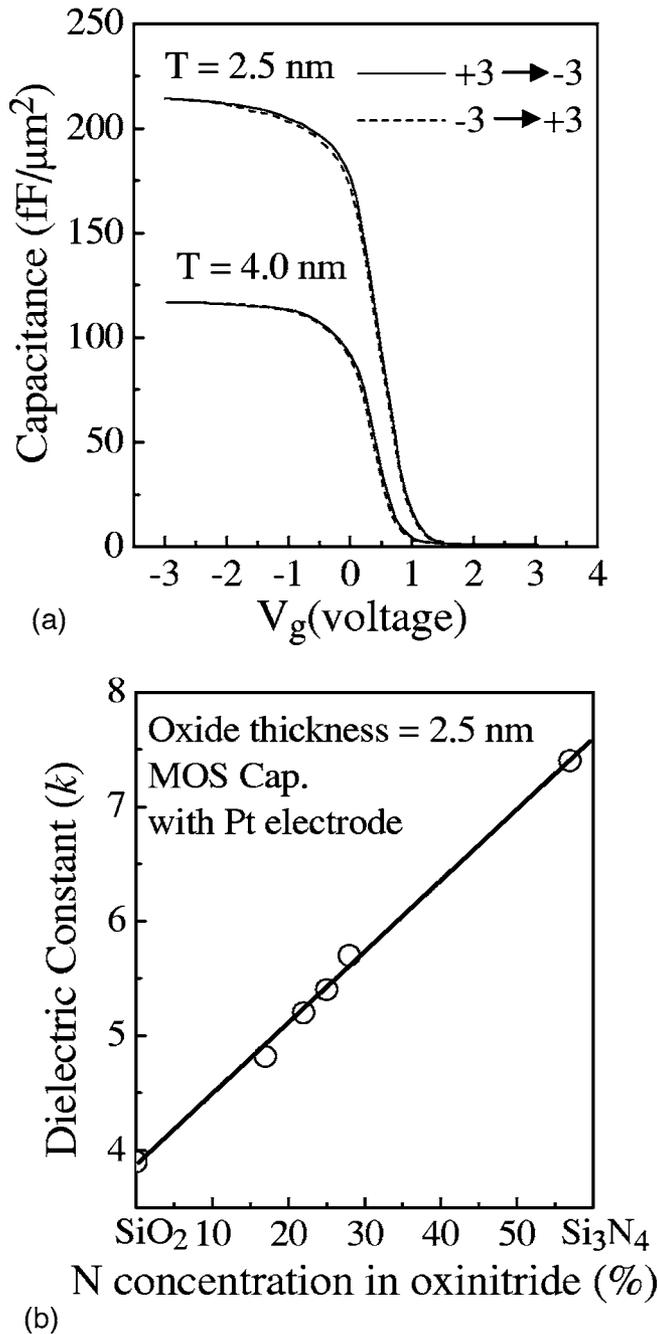


Figure 4. C-V characteristics of 2.5 and 4.0 nm thick films and dielectric constant values calculated from accumulation capacitances.

indicating that the larger amount of N incorporated in the film has significantly decreased the capacitance equivalent thickness. Therefore, a decrease in gate leakage current density can be achieved in the ultrathin gate dielectric by increasing the N content.¹⁷ The details of electrical changes and reliability caused by N incorporation will be reported elsewhere.

In summary, in ultrathin base oxides, the depth profile and chemical state of highly incorporated N atom at the SiO₂ film surface was investigated. The incorporated N species with different second-nearest neighbors are changed into a more stable state after PNA. The N₂ molecular state is generated at the film interface during the high incorporation process of N, which is unstable and diffuses out after an additional anneal. After an additional anneal as a postnitridation treatment, the film is reoxidized at the film surface to form an unstoichiometric silicon oxynitride film. The reoxidation effect is extended into the interfacial region in an ultrathin film while it is not in a thicker film. The amount of nitrogen incorporation at the film surface effectively controls the CET without degradation at the interface.

Acknowledgments

This work was partially supported by the Joint Program for Industry-Institute of Samsung Electronics and the System IC 2010 Program.

M.-H. Cho assisted in meeting the publication costs of this article.

References

1. N. Kimizuka et al., in *Technical Digest of 1999 Symposium on VLSI*, 73 (1999).
2. T. Hori, *Gate Dielectrics and MOS ULSI*, Springer-Verlag, New York (1996).
3. D. S. Ang and K. L. Pey, *IEEE Electron Device Lett.*, **25**, 637 (2004).
4. P. Kraus, K. Ahmed, T. C. Chua, M. Ersov, H. Karbasi, C. S. Olsen, F. Nouri, J. Holland, R. Zhao, G. Miner, and A. Lepert, in *Technical Digest of 2003 VLSI Symposium*, 143 (2003).
5. H. Niimi, A. Khandelwal, H. H. Lamb, and G. Lucovsky, *J. Appl. Phys.*, **91**, 48 (2002).
6. S. Mahapatra, M. A. Alam, P. B. Kumar, T. R. Dalei, and D. Saha, in *Tech. Dig. - Int. Electron Devices Meet.*, **2004**, 105.
7. H. N. Alshareef, H. Niimi, A. Varghese, M. Bavan, R. Kuan, J. Holt, P. Tiner, and R. Khamankar, *Appl. Phys. Lett.*, **86**, 132901 (2005).
8. Y. Miura, H. Ono, and K. Ando, *Appl. Phys. Lett.*, **77**, 220 (2000).
9. S. Hyun, G. H. Buh, S. H. Hong, B. Y. Koo, Y. G. Shin, U. I. Jung, J. T. Moon, M.-H. Cho, H. S. Chang, and D.W. Moon, *Appl. Phys. Lett.*, **85**, 988 (2004).
10. F. N. Cubaynes, V. C. Venezia, C. Van der Marel, J. H. M. Sniijders, J. L. Everaert, X. Shi, A. Rothschild, and M. Schaeckers, *Appl. Phys. Lett.*, **86**, 172903 (2005).
11. J. W. Keister, J. E. Rowe, J. J. Kolodziej, H. Niimi, H.-S. Tao, T. E. Maday, and G. Locovsky, *J. Vac. Sci. Technol. A*, **17**, 1250 (1999).
12. Y. K. Kim, H. S. Lee, and H. W. Yeom, *Phys. Rev. B*, **70**, 165320 (2004).
13. H. Kobayashi, T. Mizokuro, Y. Nakato, K. Yoneda, and Y. Todokoro, *Appl. Phys. Lett.*, **71**, 1978 (1997).
14. S. R. Kaluri and D. W. Hess, *J. Electrochem. Soc.*, **144**, 2200 (1997).
15. J. G. Chen, *Surf. Sci. Rep.*, **30**, 1 (1997).
16. R. Feifel, M. Andersson, G. Öhrwall, S. L. Sorensen, M. N. Piancastelli, M. Tchapyguine, O. Bjrneholm, L. Karlsson, and S. Svensson, *Chin. Phys.*, **383**, 229 (2004).
17. S. Inaba et al., in *Tech. Dig. - Int. Electron Devices Meet.*, **2002**, 651.