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Oxynitride films formed by low energy NO$^+$ implantation into silicon

J. A. Diniz and P. J. Tatsch[a]
*Departamento de Semicondutores, Instrumentos e Fotônica, Faculdade de Eng, Elétrica e Computação,
C.P. 610, Universidade Estadual de Campinas, Compinas, São Paulo 13081-970, Brazil*

M. A. A. Pudenzi
*Laboratório de Pesquisa em Dispositivos, Instituto de Fisica ''Gleb Wataghin'', C.P. 6165, Universidade
Estadual de Campinas, Campinas, São Paulo 13081-970, Brazil*

Oxynitride (SiO$_x$N$_y$) insulators have been obtained by low-energy nitric oxide ion (NO$^+$) implantation in Si substrates prior to thermal oxidation. Characterization by Fourier transform infrared (FTIR) and secondary ion mass spectrometry (SIMS) analyses reveal the presence of Si–O, Si–N, and Si–N–O bonds in the high quality 37 nm silicon oxynitride films. The dielectric constant=5.5, effective charge density=7×10^{10} cm^{-2} and breakdown *E*-fields of 3 MV/cm were determined by capacitance–voltage (*C–V*) and current–voltage (*I–V*) measurements, respectively, indicating that the SiO$_x$N$_y$ films formed are suitable gate insulators for metal-oxide-semiconductor (MOS) devices. © *1996 American Institute of Physics.* [S0003-6951(96)02441-2]

Ultrathin oxynitride films (SiO$_x$N$_y$) became a promising alternative for submicron MOS gate insulators due to their high radiation hardness, low defect density, high dielectric constant, low gate threshold shifts, and low impurity diffusion.[1–5] The improved dielectric reliability is mainly due to the pileup of the incorporated nitrogen at the SiO$_2$/Si. The Si–N bonds replace the strained Si–O bonds at the SiO$_2$/Si interface, decreasing the interface strain.[6] Several nitridation techniques have been widely investigated.[1–6] Presently, much attention has been directed on nitridation by nitrogen ion implantation.[7–12] Ion implantation provides a low temperature and highly controllable process of nitrogen implantation.[9,14,15] This work reports the experimental results of the oxynitride formation by NO$^+$ implantation at low energy (about 10 keV). Chemical bonding characteristics of the SiO$_y$N$_y$ films were determined using Fourier transform infrared spectrometry (FTIR). The nitrogen profiles at the SiO$_x$N$_y$/Si structures were measured by secondary ion mass spectrometry (SIMS). *C–V* and *I–V* measurements were performed to evaluate the insulator-semiconductor interface and bulk properties.

The silicon oxynitride layers were formed on *p*-type single-crystal Si(100) wafers with resistivities ranging from 4.9 to 9.1 Ω cm. The substrates were cleaned by RCA method, implanted with nitric oxide ions (d=2 $\times 10^{16}$ ions/cm^2 and E=10 keV), annealed at 950 °C for 20 min in nitrogen and split in two batches of samples, namely: ON1 (oxynitride 1) and ON2 (oxynitride 2)—without and with postoxidation steps, respectively. The ON2 samples were thermally oxidized at 950 °C in dry O$_2$ and annealed at 950 °C for 20 min in nitrogen. For control, bare Si substrates were thermally oxidized and annealed at the same conditions (thicknesses=24 nm). The oxynitride formation at the ON1 and ON2 structures were investigated by FTIR and SIMS analyses. Metal/oxynitride/silicon capacitors were formed by thermal 150 nm aluminum film deposition, sintered in N$_2$ +H$_2$O(v) at 440 °C for 40 min. The Al electrodes were patterned with 500 μm diameter dot mask. The wafer backside was etched in buffered HF and a 150 nm thick Al film was evaporated. *C–V* measurements at 1 MHz were performed. The static dielectric constants ϵ_{ON1} and ϵ_{ON2} were calculated from the strong accumulation capacitance C_{max}. The effective charge densities Q_{0ON1}/q and Q_{0ON2}/q were calculated directly from the flatband voltage shift V_{fb} and C_{max}. All measurements were carried out in the dark at room temperature. *I–V* characteristics were performed to determine the dielectric breakdown *E* fields.

The FTIR spectrometry was performed on the control oxide, ON1 and ON2 films [Figs. 1(a), 1(b), and 1(c), respectively] in order to evaluate chemical bonds. Absorption peaks occur at 1075 cm^{-1} (stretching mode), at 456 cm^{-1} (rocking mode), and at 810 cm^{-1} (bending mode) due to Si–O bonds.[17] Absorptions at 1255 cm^{-1} indicate the formation of high quality films.[17] Absorptions at 820 cm^{-1} (stretching mode) and at 462 cm^{-1} (wagging mode) are due to Si–N bonds.[16,18] The shapes of absorption bands from 900 to 1000 cm^{-1} are attributed to the formation of Si–N–O bonds in silicon oxynitride.[17] No absorptions at 610 cm^{-1} due to unsaturated Si–Si bonds (phonon-phonon interactions) were observed,[19] which confirm the absence of these
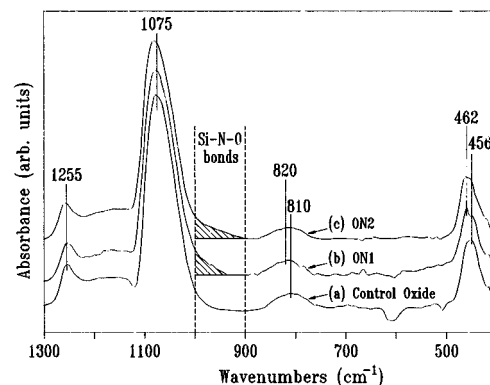

FIG. 1. FTIR spectra for (a) control oxide, (b) ON1, and (c) ON2 samples.
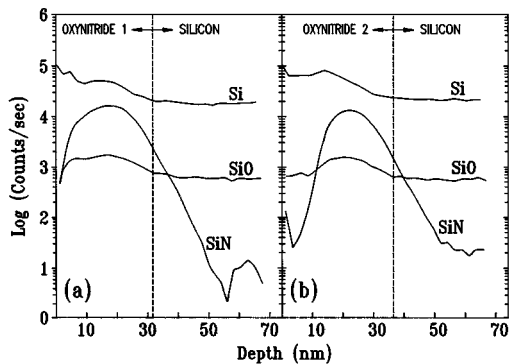
FIG. 2. SIMS profiles of ^{42}SiN, ^{28}Si, and ^{44}SiO for (a) ON1 and (b) ON2 structures.

FIG. 3. I–V characteristics (a) ON1 and (b) ON2 capacitors.

structural imperfections at the oxynitride/silicon interface. The presence of Si–N–O–Si bridges decreases the strained bonds and the Si dangling bonds at the interface. These considerations indicate the formation of a smooth interface.[20]

Figures 2(a) and 2(b) show the O_2^+ (3 keV) SIMS depth profiles of ^{42}SiN, ^{44}SiO, and ^{28}Si at ON1 and ON2 structures, respectively. These results indicate nitrogen incorporation at the insulator-semiconductor structures, formation of the SiO_xN_y layers on Si substrates and insulator film thicknesses about 32 and 37 nm, for the ON1 and ON2 samples, respectively.

The C–V characteristics of Al/SiO_xN_y/Si and Al/SiO_2/Si specimens were performed. The dielectric constants ϵ_{ON1} and ϵ_{ON2} of the SiO_xN_y films were calculated from each maximum capacitance (C_{max}) under strong accumulation conditions at 1 MHz and the SiO_xN_y thicknesses of about 32 nm (ON1 samples) and 37 nm (ON2 samples). By this method, a relative permittivity of $\epsilon_{ON1}=(4.6\pm0.1)$ and $\epsilon_{ON2}=(5.5\pm0.1)$ were found. These values, when compared with 3.82 for thermal oxides, indicate the oxynitride formation. It agrees with data of Ref. 13. The average flatband voltages V_{fb} for the structures with oxynitrides (ON1 and ON2 samples) and control oxides (CO samples) were $V_{fbON1}=-0.87$ V, $V_{fbON2}=-0.89$ V, and $V_{fbco}=-0.90$ V. From these values of V_{fb}, the average effective charge density Q_{0ON1}/q, Q_{0ON2}/q, and Q_{0co}/q were found to be about 7×10^{10}/cm^2, 6×10^{10}/cm^2, and 1×10^{11}/cm^2, respectively, indicating significant decreases of the effective charge density for the structures with oxynitride.

Figures 3(a) and 3(b) present the I–V characteristics of Al/oxynitride/Si structures, respectively, performed after successive high voltage ramp-up stress under positive gate bias. It was determined that: the dielectric breakdown regions were about 6, 10, and 6 V corresponding to breakdown E fields of 2, 3, and 3 MV/cm for the ON1, ON2, and CO samples, respectively. These electrical properties indicate that the films formed have presented higher qualities than the nitride and oxynitride films obtained by plasma enhanced chemical vapor deposition.[18]

In conclusion, the formation of thin oxynitride films by low-energy and medium-dose nitric oxide implantation can improve gate insulator integrity. The FTIR analyses revealed the presence of Si–O, Si–N–O, and Si–N bonds, the formation of a smooth SiO_xN_y/Si interface and the high quality
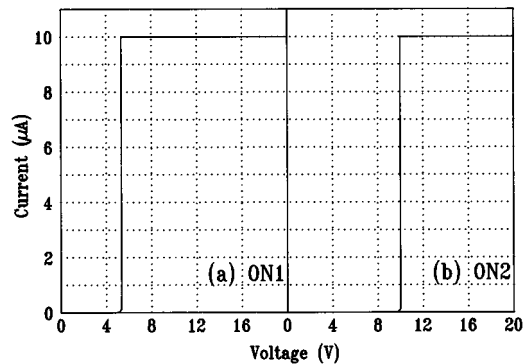
films. The SIMS results have shown the formation of oxynitride layers. Electrical properties indicated that, due to the low effective charge density and the dielectric constant of about 5.5, these high quality films can be used as gate insulator in metal-insulator-semiconductor (MIS) devices and ultralarge scale integration (ULSI) circuit applications.

[1] P. J. Tobin, Y. Okada, S. A. Ajuria, V. Lakhotia, W. A. Feil, and R. I. Hedge, J. Appl. Phys. **75**, 1811 (1994).

[2] S. Haddad and M.-S. Liang, IEEE Electron Device Lett. **EDL-8**, 58 (1987).

[3] G. D. O'Clock, Jr., M. W. Huck, M. S. Peters, M. J. Turner, B. A. Carlson, and W. Katz, IEEE Trans. Semicond. Manuf. **1**, 133 (1988).

[4] R. P. Donovan and M. Simons, J. Appl. Phys. **43**, 2897 (1972).

[5] M. Severi, L. Dori, and M. Impronta, IEEE Electron Device Lett. **EDL-6**, 3 (1985).

[6] Y.-L. Wu and J.-G. Hwu, Jpn. J. Appl. Phys. **33**, 5101 (1994).

[7] J. A. Diniz, P. J. Tatsch, L. C. Kretly, J. E. C. Querioz, and J. Godoy Fo, 10th Cong. Braz. Microelectron. Soc. Proc. **1**, 383 (1995).

[8] J. A. Diniz, P. J. Tatsch, L. C. Kretly, J. E. C. Queriroz, and J. Godoy Fo, Mater. Res. Soc. Symp. Proc. **396**, (1995).

[9] W. J. M. J. Josquin, Nucl. Instrum. Methods **209/210**, 581 (1983).

[10] C. R. Fritzche and W. Rothemund, J. Electrochem. Soc. **120**, 1603 (1973).

[11] P. Molle, C. Jaussaud, and M. Bruel, Nucl. Instrum. Methods B **55**, 860 (1991).

[12] T. Y. Chiu, W. G. Oldham, and C. Hovland, J. Electrochem. Soc. **131**, 2110 (1984).

[13] B. E. Deal, P. J. Fleming, and P. L. Castro, J. Electrochem. Soc. **115**, 300 (1963).

[14] Y. Wada and M. Ashikawa, Jpn. J. Appl. Phys. **15**, 389 (1976).

[15] M. Weidner, A. Roseler, and M. Eicher, Thin Solid Films **234**, 337 (1993).

[16] D. V. Tsu, G. Lucovsky, J. Mantini, and S. S. Chao, J. Vac. Sci. Technol. A **5**, 1998 (1987).

[17] P. Lange, H. Bernt, E. Hartmannsgruber, and F. Naumann, J. Electrochem. Soc. **141**, 259 (1994).

[18] J. Vuillod, J. Vac. Sci. Technol. A **5**, 1675 (1987).

[19] H. W. Werner, *Microelectronic Materials and Processes*, edited by R. A. Levy (Kluwer, Dordrecht, 1989), Chap. 16, p. 895.

[20] D. G. J. Sutherland, H. Akatsu, M. Copel, F. J. Himpsel, T. A. Calcott, J. A. Carlisle, D. L. Ederer, J. J. Jia, I. Jimenez, R. Perera, D. K. Shuh, L. J. Terminello, and W. M. Tong, J. Appl. Phys. **78**, 6761 (1995).