High quality of ultra-thin silicon oxynitride films formed by low-energy nitrogen implantation into silicon with additional plasma or thermal oxidation


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Abstract

Silicon oxynitride (SiO\textsubscript{x}N\textsubscript{y}) insulators have been obtained by low-energy molecular nitrogen ion (N\textsuperscript{2+}) implantation in Si substrates prior to thermal or high density O\textsubscript{2} ECR (electron cyclotron resonance) or N\textsubscript{2}O RP (remote plasma) plasma oxidation at temperatures of 20°C and 350°C, respectively. Characterization by Fourier transform infrared (FTIR) analyses reveals the high structural quality and very low Si–N bond concentration of oxynitride films. The film thicknesses between 2.5 and 12 nm were found by ellipsometry using a fixed refractive index of 1.46. MOS capacitors, with Al electrodes and final sintering time at 420°C for 20–30 min in forming gas, were fabricated. A relative dielectric constant of 3.9 was adopted to extract the effective charge densities from capacitance–voltage (C–V) curves, resulting in values between 4×10\textsuperscript{10} and 6×10\textsuperscript{11} cm\textsuperscript{-2}. Breakdown electric fields from 9–26 MV/cm were obtained from current–voltage (I–V) measurements. These results indicate that the obtained SiO\textsubscript{x}N\textsubscript{y} films are suitable gate insulators for metal-oxide-semiconductor (MOS) devices. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Silicon oxynitride (SiO\textsubscript{x}N\textsubscript{y}) became a promising material for sub-micron MOS ultra-thin gate insulators due to its 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 pile-up of the incorporated nitrogen in the vicinity of the SiO\textsubscript{2}/Si interface. The Si–N bonds replace the strained Si–O bonds at the SiO\textsubscript{2}/Si interface, decreasing the interface strain [6]. Several silicon oxide nitridation techniques have been widely investigated [1–6]. Nowadays, much attention has been directed on nitridation by nitrogen or nitric oxide ion implantation [7–13]. Ion implantation provides a low temperature and highly controllable process of nitrogen incorporation [9,14]. Usually, prior to nitridation, a conventional or rapid thermal oxidation has been used to grow...
the ultra-thin silicon oxide on silicon substrates at temperatures higher than 800°C. These high temperatures are necessary to activate the process. High density plasma oxidation has become an alternative because it is performed at low temperature, less than 400°C, which is important to reduce the thermal budget of the device manufacturing [15,16]. The high density plasma can be obtained in plasma reactors, with microwave power generator (frequency of 2.45 GHz), such as the electron cyclotron resonance (ECR) systems, which generate the reactive oxygen species [15,16].

This work reports the experimental results of oxynitride formation by $N_2^+$ implantation at low energies (about 5 keV) prior to thermal or electron cyclotron resonance (ECR) plasma or microwave remote plasma (RP) oxidation. The chemical bonds and quality of the SiO$_x$N$_y$/Si structures were measured by Fourier transform infra-red spectrometry (FTIR). The film thickness was determined by ellipsometry. $C$–$V$ and $I$–$V$ measurements were performed to evaluate the insulator–semiconductor interface and bulk properties.

2. Experimental

The silicon oxynitride layers were formed on p-type single-crystal Si(1 0 0) wafers with resistivities ranging from 11 to 22 Ω cm. The substrates were cleaned by RCA method and split into three batches of samples, namely: OxyNitride formed by ECR plasma oxidation (ONECR), OxyNitride formed by RP plasma oxidation (ONRP) and OxyNitride formed by thermal oxidation (ONTOX). All samples were implanted with 5 keV $N_2^+$ ions, dose of $1 \times 10^{15}$ ions/cm$^2$ and annealed at 950°C for 20 min in nitrogen. Following, the ONECR and ONRP samples were oxidized by ECR (O$_2$ flows of 40 sccm, microwave power of 500 W, RF power of 20 W, pressure of 10 mTorr, temperature of 20°C and time of 30 min) and RP (N$_2$O flows of 125 sccm, microwave power of 600 W, pressure of 1.5 Torr, temperature of 350°C and time of 30 min) plasma, respectively. The ONTOX samples were thermally oxidized at 950°C for 5 min in dry O$_2$ and annealed at 950°C for 20 min in nitrogen. For control, bare Si substrates were oxidized in the same conditions by ECR or RP plasma oxidation or thermally oxidized and annealed. These control oxide samples were split into three batches, namely: Control Oxide formed by ECR plasma oxidation (COECR), Control Oxide formed by RP plasma oxidation (CORP) and Control Oxide formed by thermal oxidation (COTOX).

MIS capacitors were fabricated by e-beam evaporation of 0.15 μm thick aluminum film, patterning of 150 μm diameter dots and sintering in forming gas at 420°C for 10–30 min. The wafer backside was etched in buffered HF and a 0.15 μm thick Al film was evaporated. $C$–$V$ measurements (BOONTON 72-B capacimeter) were performed at 1 MHz. The thermal oxide static dielectric constant of 3.9 was adopted for calculations for parameter extraction. The effective charge densities $Q_0/q$ were calculated directly from the flatband voltage shift $V_{fb}$. $I$–$V$ characteristics were measured to determine the dielectric breakdown $E$-fields.

Thicknesses ($t_{ox}$) of the films were measured by ellipsometry (Rudolph Research Auto EL NIR-3 ellipsometer). A fixed wavelength of 632.8 nm and an incidence angle of 70° were used. A thermal silicon oxide refractive index of 1.46 and a complex refractive index $N_i$ of silicon substrate of 3.858–i.0.018 were used.

The chemical bonds and quality of SiO$_x$N$_y$/Si structures were evaluated by FTIR spectrometry (FTS-40 BIO-RAD).

3. Results and discussions

The average values of film thickness of COECR, ONECR, CORP, ONRP, COTOX and ONTOX samples were found to be 8.1, 8.1, 2.5, 5.3, 11.7 and 5.6 nm, respectively, indicating the formation of ultra-thin and thin insulators. Nitridation by $N_2$ ion implantation leads to an inhibition in the thermal oxidation of Si, an enhancement in the thermal oxidation in a microwave remote plasma ambient at intermediate temperature (350°C) and does not affect the oxidation rate in a high density ECR plasma at room temperature.
FTIR spectra of the control oxide samples are shown in Figs. 1(a), (c) and (e) and of the three oxynitrides are shown in Figs. 1(b), (d) and (f). From the spectra of Fig. 1, absorption peaks at 1070 cm$^{-1}$ (stretching mode), at 458 cm$^{-1}$ (rocking mode) and at 810 cm$^{-1}$ (bending mode) due to Si–O bonds in silicon oxide are observed [17]. Peaks at 1256 cm$^{-1}$ have been attributed to high quality oxide [17], indicating the high quality of our obtained films. Due to the ultra-thin oxide formation by plasma oxidation in the RP reactor (CORP samples), the FTIR analysis quality of Fig. 1(e) is not so good. Even so, by comparing the spectra of Figs. 1(e) and (f), a better structural film formation is observed for the ONRP oxynitrides compared to the CORP oxide. From the spectra of oxynitrides (Figs. 1(b), (d) and (f)), the following can be concluded: absorption occurs at 835 cm$^{-1}$ (stretching mode) due to Si–N bond for ONTOX samples [18] and distinct additional shapes of absorption band from 850 to 1000 cm$^{-1}$ are attributed to the formation of O–Si–N bonds [17], indicating the oxynitride formation, but with low nitrogen incorporation.

Figs. 2(a)–(c) present the $C–V$ characteristics of Al/SiO$_x$N$_y$/Si capacitors. The $Q_0/q$ average effective charge densities were found to be about $6 \times 10^{11}$ cm$^{-2}$ (Fig. 2(a)), $4 \times 10^{10}$ cm$^{-2}$ (Fig. 2(b)) and $1 \times 10^{11}$ cm$^{-2}$ (Fig. 2(c)) for samples ONTOX, ONECR and ONRP, respectively, for sintering times between 20 and 30 min. So, a significant decrease of the effective charge density for the

Fig. 1. FTIR spectra of (a) COTOX, (b) ONOX, (c) COECR, (d) ONECR, (e) CORP and (f) ONRP.
structures with oxynitride formed by ECR O₂ plasma oxidation (ONECR samples) was observed. Fig. 3 shows the average effective charge densities for all samples as a function of sintering time. The lowest charge densities were observed for times between 20 and 30 min and the best result as discussed previously was presented by the ONECR capacitors. In general, a lower interface charge density is observed on oxynitride samples compared to its silicon oxide control samples.

Fig. 4 presents the I–V characteristics performed after successive high voltage ramp-up stress under positive gate bias. It was determined that: the dielectric breakdown voltages were about 14, 8 and 7 V corresponding to average breakdown E-fields of 26, 10 and 13 MV cm⁻¹ for the ONTOX, ONECR and ONRP samples, respectively. For the control oxides, the dielectric breakdown voltages were about 14, 9 and 18 MV cm⁻¹ for the COTOX, COECR and CORP samples, respectively. Except for the remote plasma case, the oxynitride films present higher breakdown compared to its silicon oxide control samples. This indicates that the presence of low nitrogen concentration at the insulator–semiconductor interface decreases the strain bonds and increases the integrity of the films. The exception for the remote
plasma samples can be explained by the fact that the control oxide (CORP) thickness was very thin, which leads to higher breakdown $E$-fields [19].

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, by implantation into silicon and by rapid thermal nitridation in NO ambient [20–22].

4. Conclusions

Fabrication of high quality thin oxynitrides by means of low-energy $N_2^+$ ion implantation on a Si surface followed by three different oxidation processes has been performed. From the study, the following main conclusions are obtained:

- nitridation by $N_2^+$ ion implantation prior to thermal or plasma oxidation improves the quality of the dielectric film in terms of effective interface charge density and breakdown electric field;
- room temperature in a high density ECR plasma results in the lowest effective charge density, compared to the other two oxidation processes;
- nitridation by $N_2^+$ ion implantation leads to an inhibition in the thermal oxidation of Si, an enhancement in the thermal oxidation in a microwave remote plasma ambient at intermediate temperature (350°C) and does not affect the oxidation rate in a high density ECR plasma at room temperature.

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