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Thermally grown silicon nitride films for high-performance MNS devices

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Amorphous and uniform silicon nitride films with thicknesses of less than 100 Å have been thermally grown on silicon wafers by employing purified ammonia gas. The films are much denser than conventional CVD Si_3N_4 films. The MNS (metal–thermal nitride–silicon) structures have very low N_{ss} in the order of 3×10^{10} $cm^{-2}eV^{-1}$ and an effective electron mobility of larger than 800 cm²/V sec in the fabricated *n*-channel MNSFFT.

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Over the years, it has been recognized that thermal nitridation of silicon wafers yields polycrystalline silicon nitride in the form of either small or microcrystals.[1–3] Recently, the authors have found that amorphous and uniform silicon nitride films can be thermally grown by eliminating oxidant impurities to less than 1 ppm at temperatures ranging from 1200 to 1300 °C.[4,5] The fact implies that nitrogen radicals, the amount of which is much more than that of oxygen, are required for the nitridation which exceeds oxidation in reaction speed.

This paper describes that stoichiometric silicon nitride films can be grown on silicon wafers at relatively low temperatures by employing ammonia gas instead of nitrogen because a lot of active nitrogen radicals are expected to be easily produced. Growth conditions, structure, and fundamental properties of thermal silicon nitride films grown in ammonia gas have been studied with metal-nitride-silicon (MNS) diodes and an *n*-channel MNS transistor.

Preparation of silicon wafers [CZ, *p* type, (100), 3–5 Ω cm, boron doped] was as follow: degreasing in an organic solvent, boiling in sulfuric and nitric acide, etching in hydrofluoric acid, and rinsing in deionized water. The wafers were completely dried in nitrogen ambient and were put into a quartz tube. An inert gas such as argon was flowing through the tube. When the temperature of the wafer increased to a set point, ammonia gas was substituted for the inert gas. Both the inert and the ammonia gases were fully purified by eliminating oxidant impurities to less than 1 ppm. Thermal nitridation was feasible at temperatures ranging from 950 to 1300 °C. Film thickness was within 100 Å because the growth was predominantly limited by diffusion of nitrogen radicals. The surface of the thermal nitride film was as smooth as that of a chemically polished silicon wafer. No nonuniformities were observed by electron microscopy over a wide range of growth conditions. It was deduced from a halo pattern of electron diffraction that the film structure was amorphous. According to the results of structural analyses by Auger electron spectroscopy, as ion microanalyzer, and ellipsometry, the thermal nitride was expected to be nearly stoichiometric Si_3N_4.

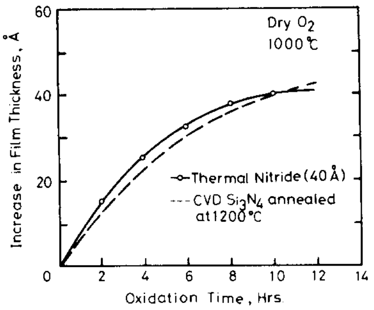

FIG. 1. Typical relation between change of total film thickness and oxidation time in dry oxygen at 1000 °C. The 40-Å-thick nitride film was grown in ammonia gas, which is compared with the Si_3N_4 film grown by Fränz *et al.* (Ref. 6).

Masking effect of the nitride films against oxidation in dry oxygen was examined for a comparison with a CVD Si_3N_4 film. Figure 1 shows a typical relation between the change of total film thickness and oxidation time at 1000 °C. Although the thickness gradually increases with time by oxidation of the nitride film its change is only 40 Å after 10 h. Under the same oxidation conditions the thickness increase of a CVD Si_3N_4 film which was deposited at 900 °C using an SiH_4—NH_3 system was three times larger than the value mentioned above. The increase rate of film thickness in the CVD film gradually decreased with increasing oxidation time. This is because the CVD film was densified through annealing at the oxidation temperature. A densified CVD film which was fully annealed at 1200 °C [6] was chosen for a comparison. It is clear that the thermal nitride film is as dense as the fully densified CVD film.

Electrical characteristics of the MNS diodes with aluminum gates 400 μm in diameter were measured. The relative dielectric constant of the nitride film was

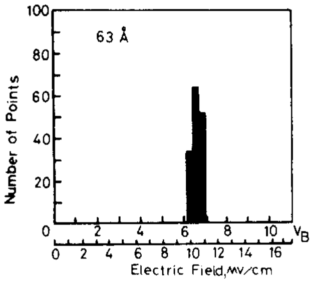

FIG. 2. Histogram of dielectric breakdown voltages of the thermal nitride film with thickness of 63 Å.

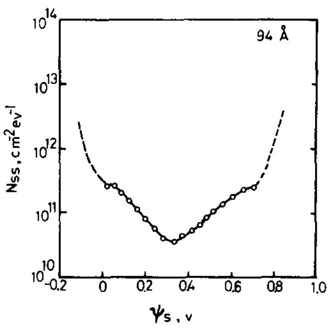

FIG. 3. Distribution of surface-state density N_{ss} with respect to surface potential Ψ_s, determined from measurements by the quasistatic technique.

about 6.0, which is almost 50% larger than the value of thermal SiO_2 films. Figure 2 shows a typical histogram of dielectric breakdown voltages of the nitride film with a thickness of 63 Å, which was measured by applying negative voltage to each gate of the MNS diodes. More than 150 dots of gates were subjected to the measurement from edge to edge over the 2-in wafer. Breakdown uniformity is much better than ± 5% within the wafer. On the average, the maximum electric field is 10.5 MV/cm, which seems to be an adequate value in Si_3N_4.[2]

Capacitance-voltage characteristics of the MNS diode were very stable and showed no hysteresis loop with a field stress of larger than ± 5 MV/cm. The fixed insulator charge per unit area Q_{ss} was typically 5×10^{11} charges/cm^2 calculated from the C-V curve. The flatband voltage V_{FB} was -0.9 V. Although these values seem relatively large, the work-function difference between the Al gate and the Si substrate (-0.95 V) and some charges located at the interface between the Al gate and the nitride film were mostly predominant. The surface-state density N_{ss} was determined by employing the quasistatic capacitance-voltage technique.[7] The result is shown in Fig. 3. The N_{ss} is of the order of 3×10^{10} cm^{-2} eV^{-1} at the center of the Si band gap. The distribution of N_{ss} with respect to surface potential is almost similar to those of clean Si-SiO_2 systems with Al gates[8] or Si gates.[9]

The nitride film with a thickness of 95 Å was incorporated with the silicon gate technology for a realization of the n-channel MNS field-effect transistor (FET) with higher performance. A poly-Si gate deposited on the nitride film can be fully doped by impurities for its low resistivity since the very thin nitride film acts as a perfect mask against the diffusion. The channel length and width of the fabricated MNSFET were 4 and 20 μm, respectively. The depth of source and drain junctions was 0.4 μm, which was formed by phosphorus diffusion from a PSG film. A photograph of drain characteristics by a transistor curve tracer is shown in Fig. 4. The negative threshold voltage of -0.15 V is due to the substrate with a relatively low acceptor concentration of 3×10^{15} cm^3 and a thin-film thickness of 95 Å. Enhancement mode operation would be easily attained, for example, by employing channel doping by ion implantation. A very large transconductance of about 2 mmho, which was calculated at gate and rain voltages of 1 and 4 V, respectively, yields an effective electron mobility of larger than 800 cm^2/V sec. This practical application would be useful as a short-channel FET is LSI because the thinner gate insulator film with a larger dielectric constant is effective to eliminate so-called short-channel effects[10] and to decrease its occupied area.

FIG. 4. I-V characteristics of the MNSFET's which employs the thermal nitride film with thickness of 95 Å as a gate insulator.

In conclusion, thermally grown silicon nitride films with high density have been uniformly obtained on silicon wafers by employing fully purified ammonia gas. Although the film thickness is limited to less than 100 Å, electrical properties are excellent and almost free from instability which is caused by carrier trapping at a silicon-nitride interface. Characteristics of the MNS structures presumably promise that the thermal nitride films are utilized as an alternate of thin SiO_2 films.

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