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Stability of nitrided silicon dioxide deposited by reactive sputtering

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The electrical properties of nitrided silicon dioxide formed by reactive sputtering in $Ar/O_2/N_2$ plasma from the SiO_2 target have been studied. The nitrogen mixing ratio was varied from 0% to 15%, with the argon mixing ratio kept at 80%. It is found that as more nitrogen is incorporated, the leakage current increases for electron injection from both aluminum and silicon. By nitrogen reactive sputtering, the interface states generation during constant current stress is greatly reduced in comparison with oxide sputtered in only an Ar/O_2 gas mixture. A mixture ratio of $Ar/O_2/N_2$ equal to 80:15:5 is found to give optimum oxide quality with good resistance to interface states generation and low leakage current. © *1995 American Institute of Physics.*

Sputtered silicon dioxide has been considered as a suitable gate insulator for thin film transistors for display technologies.[1] Good breakdown and interface properties were reported for sputtering of oxide in oxygen containing gas mixture (Ar/O_2).[2,3] By annealing of the sputtered oxide, interface properties can be improved.[4,5] As reported by Lucovsky *et al.*,[6] in order to make full use of the deposited oxide, there is a need for moderately high temperature (800–900 °C) postdeposition sintering. We have also found that stability of the sputtered oxide can be improved by optimization of sputtering conditions.[7]

In order to improve thermal oxide hardness against irradiation and hot carrier injection, incorporation of nitrogen in oxide from NH_3 or N_2O has been practiced recently.[8–10] It may be expected that nitrogen can play a similar role if introduced in the sputtered oxide by the reactive sputtering process, and this letter presents results on the electrical properties of such a gate oxide.

The oxide was sputtered (22 to 28 nm) in $Ar/O_2/N_2$ plasma on a *p*-type (100) silicon wafer from a SiO_2 target in an rf sputtering system. A nitrogen mixing ratio $N_2/(Ar+O_2+N_2)$ was estimated by (nitrogen flow rate)/(total flow rate) and was varied from 0% to 15%, with the argon mixing ratio constant (80%). Sputtering pressure was fixed at 0.3 Pa, and sputtering power was about 2 W/cm^2. The deposition temperature was 300 °C. Postdeposition sintering was carried at 900 °C in N_2 for 20 min. After aluminum patterning, samples were annealed in forming gas at 400 °C for 10 min. MOS capacitors (of area 1.3×10^{-4} cm^{-2}) were evaluated by $I-V$ and high frequency capacitance measurements. Constant current stress due to Fowler–Nordheim tunneling was applied for the degradation study.

A typical current–electric field behavior of nitrided sputtered oxides is illustrated in Fig. 1. It shows that by adding nitrogen to the sputtered oxide, the leakage current increases. This property is common for thermal nitrided oxides.[8,10] It is observed for both electron injection from aluminum and silicon. At higher fields (>11 MV/cm), the current rises more rapidly, which is probably related to positive charge generation and reduction of injection barrier height for electrons.[5,11]

Breakdown properties were studied by applying a negative staircase voltage (0.1 V/step) on the gate electrode, driving MOS capacitors in accumulation. Breakdown was considered as the point of irreversible current increase. Weibull plots of breakdown events of nitrided and only Ar/O_2 sputtered oxides are presented in Fig. 2. As the nitrogen mixing ratio increases, the breakdown field is lowered. However, Ar/O_2 sputtered oxide has a "soft" knee in the cumulative breakdown curve. In contrast, the heaviest nitrided sample has a very steep cumulative breakdown curve, indicating a tight breakdown distribution. It can be supposed that incorporated nitrogen reduces microdefect density and improves the current uniformity. A similar result is reported on thermal oxide nitrided by NH_3.[10]

After applying a constant current stress (Al electrode negative), the charge trapped in the oxide is detected by the variation of the midgap voltage with time (determined from the high frequency $C-V$ curve). For all nitrogen mixing ratios, Fig. 3 shows there is an initial period of electron trapping, after which the generation of positive charge becomes more dominant. Interestingly, the amount of injected electron charge at the turnaround point does not depend on the nitrogen mixing ratio. A small amount of nitrogen (5%) shifts the midgap voltage to more positive values in comparison to only Ar/O_2 sputter oxide. It suggests increased electron trapping, which is the usual observation for lightly nitrided oxides.[8,10] However, at higher nitrogen flow rates the electron trapping in the oxide is lowered.

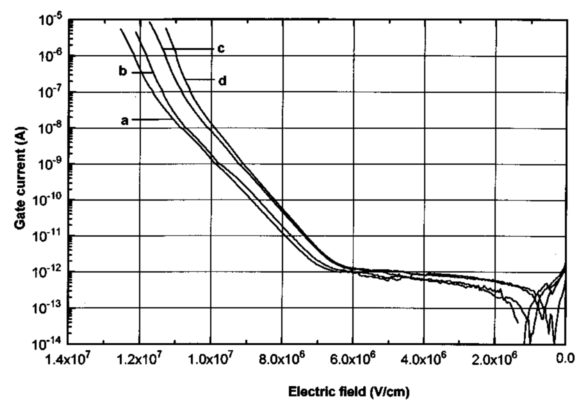

FIG. 1. Gate current dependence on electric field (electron injection from aluminum). Nitrogen mixing ratio: (a) 0%; (b) 5%; (c) 10%; and (d) 15%.

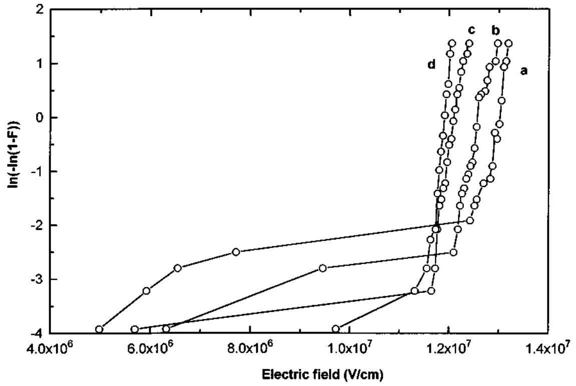

FIG. 2. Weibull plots of breakdown field distribution (electron injection from aluminum). Nitrogen mixing ratio: (a) 0%; (b) 5%; (c) 10%; and (d) 15%. *F*: number of failed capacitors over the total number of tested capacitors.

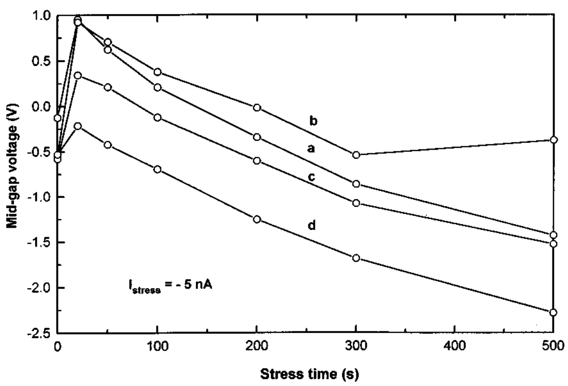

FIG. 3. Change in midgap voltage with duration of constant current stress (electron injection from aluminum). Nitrogen mixing ratio: (a) 0%; (b) 5%; (c) 10%; and (d) 15%.

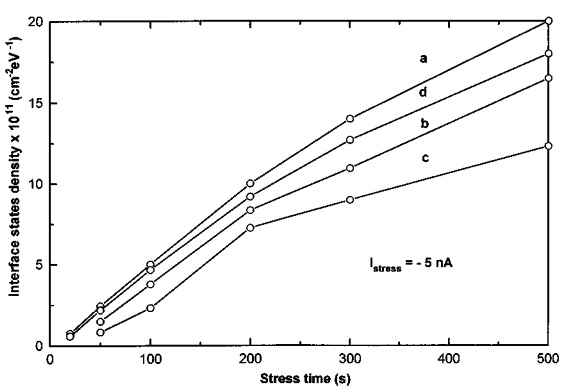

FIG. 4. Interface state density dependence on duration of constant current stress (electron injection from aluminum). Nitrogen mixing ratio: (a) 0%; (b) 5%; (c) 10%; and (d) 15%.

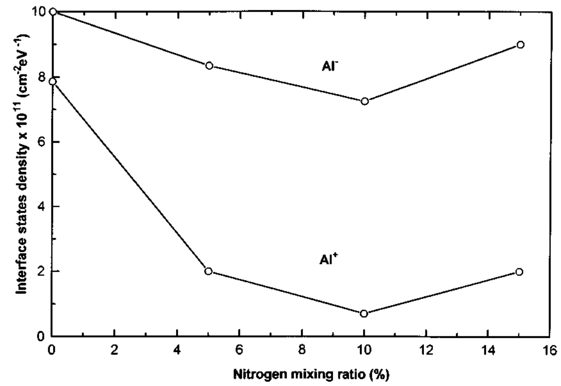

FIG. 5. Interface state density dependence on nitrogen mixing ratio. Stress time: 200 s; Al^+: electron injection from silicon (5 nA) and Al^-: electron injection from aluminum (−5 nA).

Nitridation by reactive sputtering also shows that incorporated nitrogen remarkably reduces generation of interface states after negative and positive current stress (Figs. 4 and 5). Interface states are calculated from the high frequency $C-V$ curve by Terman's method.[13] The presented value is the minimum interface state density in the silicon band gap. The generation of interface states is at a minimum at a 10% nitrogen mixing ratio for positive and negative stress. For electron injection from silicon, the interface state density is about ten times lower for 10% nitrided oxide compared with non-nitrided oxide. There is about a 75% reduction in interface state density in 10% nitrided oxide for electron injection from aluminum. Similar asymmetrical behavior of the generation of interface states after constant current stress is observed in thermal nitrided oxide as well.[10] The beneficial role of nitrogen should be attributed to the replacement of some Si–O bonds with stronger Si–N bonds.[9] We can suppose that at a 5%–10% mixing ratio, a $Si_xN_yO_z$ layer is formed at the Si/SiO_2 interface that has a reduced strain gradient due to the presence of the Si–N bond, and therefore better resistance to hot electron injection.[9]

In summary, incorporation of a controlled amount of nitrogen in reactive sputtered oxide can give a hardened oxide–silicon interface. In order to properly exploit this advantage, care should be taken regarding the effect of the nitrogen mixing ratio on leakage current, trapping sites, and breakdown voltage. From our experimental results, the $N_2/Ar/O_2$ ratio of 5:80:15 is considered as optimum, giving the most desirable leakage current and resistance to interface state generation.

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