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Process dependence of breakdown field in thermally nitrided silicon dioxide

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We have studied the dependence of breakdown field in nitrided oxides on nitridation conditions. Nitridation improves the breakdown field of the oxides. In an attempt to explore the cause of the improved breakdown, the breakdown field was related with electron-trap density and refractive index (which increases with nitrogen concentration in the oxide). Our results suggest that the enhanced breakdown field of nitrided oxides is mainly due to incorporation of nitrogen, which results in structural changes in the nitrided oxide.

I. INTRODUCTION

The growth of good-quality silicon dioxide with high breakdown strength is, as yet, a major preoccupation with device technologists. In particular, in very-large-scale integration (VLSI) circuits, the breakdown of oxide layers poses a limit to the yield and reliability of circuits.\(^1\) The breakdown of silicon dioxide in metal-oxide-semiconductor (MOS) devices has been studied by many researchers. Several physical models have been proposed for explaining the breakdown of silicon dioxide, such as impact ionization, thermal runaway, positive-charge buildup, and electron trapping.\(^2\)\(^-\)\(^5\) It has also been reported in the literature that the breakdown voltage of dry oxides is enhanced by a large number of electron traps.\(^6\)

Recently, it has been reported that thermal nitridation of SiO\(_2\) improves breakdown strength.\(^7\) Although this enhanced breakdown voltage of nitrided oxides has been explained by a few researchers, there seems to be a disagreement over the reasons. Lal, Dong, and Harstein\(^8\) have suggested that the improvement in breakdown voltage is due to a large number of electron traps in nitrided oxides. Pan\(^9\) and Yankova, DoThanh, and Balk\(^10\) have suggested that it is due to a reduction in local defect sites due to nitridation. Ito et al.\(^11\) explained the improvement by invoking the surface nitrided layer which forms during nitridation and acts as a barrier against contamination. A simple model can be postulated\(^8\) for the improvement in breakdown field based on the presence of a large number of electron traps. It is known that positive-charge buildup in hole traps near the interface during high-field stressing leads to breakdown.\(^12\)\(^,\)\(^13\) If a large number of electron traps were present in the insulator, some of them would get filled up by electrons injected during high-field stressing. This would result in a buildup of negative charge, which counters the positive-charge buildup at the interface and inhibits further injection of electrons. This results in breakdown occurring at higher fields compared to an insulator without the filled electron traps. Of course, an insulator with a fewer number of hole traps should also show improved breakdown.

We have fabricated nitrided oxides under different processing conditions which have different electron-trap densities and nitrogen content. We were in a position to explore whether the enhanced breakdown voltage in nitrided oxides is determined by the number of electron traps or the nitrogen content in the oxide. Breakdown studies were carried out using ramp-voltage-stressed current-voltage (I-V) measurements. Constant-voltage-stressed current-time (I-t) measurements were performed to determine the current decay. We have found from our measurements that electron traps do not play a dominant role in improving breakdown voltage. On the other hand, the dependence of breakdown voltage on refractive index of the oxide is more pronounced, indicating that the enhanced breakdown voltage is due to incorporation of nitrogen during nitridation, which results in structural changes in the oxide.

II. EXPERIMENTAL DETAILS

The MOS capacitors used in this study were fabricated on p-type (100) silicon wafers with resistivities of 0.15–0.25 \(\Omega\) cm. 300–400-Å-thick dry oxides were thermally grown at 1000 °C, followed by an anneal in nitrogen at 1000 °C for 30 min. Nitridation was carried out at various ammonia contents (25%, 40%, 60%, and 100% NH\(_3\) in nitrogen) at 1000, 1050, and 1100 °C for 30, 60, and 120 min, respectively. A total of 36 different nitridation conditions were used. Post-nitridation anneal in nitrogen was carried out for 30 min at the nitridation temperature. Aluminum was deposited in an e-beam evaporation system for gate and back contacts. Gate contacts of 1 mm\(^2\) were defined by photolithography. Finally, a post-metal anneal was performed in \(H_2\) at 450 °C for 30 min.

The refractive index measurements were carried out using a Rudolph Auto EL-II ellipsometer. The ramp-voltage-stressed I-V technique was used to measure the breakdown voltage. Transient current was measured to find the rate of decay of current in nitrided oxides. The measurements were performed using a Keithley 617 electrometer and HP 9826 instrument controller.

III. RESULTS AND DISCUSSION

A. Ramp-voltage-stressed I-V

Typical ramp-voltage-stressed I-V characteristics for dry oxide and oxides nitrided at different times are shown in Fig. 1. The breakdown voltage is defined as the voltage...
FIG. 1. $I-V$ curves for dry oxide and oxides nitrided at 1050 °C and 100% NH$_3$. (O) dry oxide, (X) 30 min, (A) 60 min, and (□) 120 min.

at which a current of $10^{-5}$ A (corresponding to $10^{-3}$ A/cm$^2$) flows through the capacitor. Breakdown voltage increases with increase in nitridation time as shown in Fig. 1. Moreover, in nitrided oxides the current is less for a given voltage than for dry oxide and decreases with increase in nitridation time. This is likely to be because of buildup of trapped electrons in nitrided oxides. Similar curves were observed for other nitridation temperatures and NH$_3$ content in ambient. Lai and co-workers have also observed similar $I-V$ curves for their nitrided oxides and suggested that this is due to electron trapping. Electron traps in nitrided oxides are large in number and are observed to be dependent on nitridation conditions. The breakdown distributions for silicon dioxide before and after nitridation at 1050 °C with 100% NH$_3$ for different nitridation times are shown in Fig. 2, which shows the percentages of breakdown for a total of about 40 capacitors on each wafer for different fields. This shows that after nitridation, the breakdown field increases with increase in nitridation time. The percentage of breakdown events at high fields has also increased with nitridation time, resulting in a higher distribution compared to dry oxides. The distribution of breakdown behavior for oxides nitrided at other temperatures and ammonia content is similar to that of Fig. 2.

Current transients at a constant applied voltage were measured for dry and nitrided oxides. These measurements were performed to find the rate of decay of current in nitrided oxides and to check whether the smaller currents for nitrided oxides seen in the $I-V$ characteristics are due to electron trapping. Figure 3 shows the current in the oxide as function of time for dry oxide and nitrided oxides subjected to a constant field of 7 MV/cm. The rate of decay in current for dry oxide is very small even up to 30 min. For nitrided oxides, the rate of decay is high and also depends on nitridation time as shown in Fig. 3. For any given time the current in nitrided oxides is less than dry oxide and decreases with increase in nitridation time. The results of $I-V$ and $I-t$ measurements indicate that electron traps do affect the current flowing in the insulator. It is quite possible that they affect breakdown also.

B. Correlation between breakdown field and electron-trap densities

Our nitrided oxides have a large number of electron traps whose number is dependent on nitridation conditions. The number of electron traps increases with nitridation time, whereas it decreases with increase in nitridation temperature and NH$_3$ content. We were in a position to correlate the breakdown fields of nitrided oxides with their respective electron-trap densities obtained from avalanche-injection measurements.

FIG. 2. Breakdown-field distribution histogram for dry oxide and nitrided oxides.

FIG. 3. Plot of $I-t$ curves for dry oxide and nitrided oxide at 1000 °C and 100% NH$_3$.  

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The average breakdown field is plotted as a function of nitridation time for different nitridation temperatures for 100% NH\textsubscript{3} nitrided oxides in Fig. 4. The average in this figure and subsequent figures is taken over 3\(\times\) capacitors. After nitridation the breakdown fields were found to increase with nitridation time and nitridation temperature. The increase in breakdown field for 60 min of nitridation is marginal compared to 30 min; however, for 120 min it increases substantially again. Similar trends in breakdown were observed for oxides nitrided with 40% NH\textsubscript{3} and 60% NH\textsubscript{3}. With increasing NH\textsubscript{3} content in the ambient the breakdown field of the nitrided oxide is also found to increase as shown in Fig. 5. These results clearly indicate that the breakdown field of nitrided oxide depends on nitridation conditions such as time, temperature, and NH\textsubscript{3} content in the ambient.

As mentioned earlier, we attempted to resolve the disagreement over the models for enhanced breakdown field of SiO\textsubscript{2} after nitridation using our nitrided oxides having different electron-trap densities. Electron-trap density was found from the avalanche-injection measurements as reported earlier.\textsuperscript{15} The voltage applied during the avalanche injection was a sine wave of 30–40-V peak at 150 kHz, and the injection current was kept constant at 2.2\(\times\)10\textsuperscript{-5} A/cm\textsuperscript{2}. The flatband voltage shift \((\Delta V_{FB})_E\) due to electron trapping increases with time of injection and quickly saturates within a few minutes at a value \((\Delta V_{FB})_{E,\text{sat}}\).\textsuperscript{15} The number of electron traps may be estimated from the initial rate of increase of \((\Delta V_{FB})_E\). However, in our case, we prefer to use the value of \((\Delta V_{FB})_{E,\text{sat}}\) because this is proportional to the number of filled electron traps in the steady state, which is what will affect the breakdown voltage. The breakdown field and corresponding shift in flatband voltage due to electron trapping \((\Delta V_{FB})_{E,\text{sat}}\) were plotted with nitridation time, temperature, and NH\textsubscript{3} content as shown in Figs. 6(a), 6(b), and 6(c), respectively. It is observed from Fig. 6(a) that the breakdown field increases as does \((\Delta V_{FB})_{E,\text{sat}}\) with nitridation time. For changes in other nitridation conditions (temperature and NH\textsubscript{3} content in the ambient) as shown in Figs. 6(b) and 6(c), the breakdown field and \((\Delta V_{FB})_{E,\text{sat}}\) change in opposite directions. A plot of breakdown field versus number of filled electron traps for different nitrided oxides is shown in Fig. 7. No correlation is observed between the number of filled electron traps and breakdown voltage of nitrided oxides. These results suggest that the improved breakdown field of nitrided oxides is not determined primarily by electron-trap density.

C. Correlation between breakdown field and refractive index

It is reported that with increase in nitridation time and temperature, the amount of nitrogen increases at the surface, bulk, and interface of the oxide.\textsuperscript{16} In our nitrided oxides the relative amount of nitrogen was evaluated from refractive-index and etch-rate measurements. Electron spectroscopy for chemical analysis and IR measurements were carried out only on a few nitrided oxide samples which clearly indicated the presence of nitrogen incorporation. The increase in refractive index of oxides after nitridation indicates incorporation of nitrogen in the films. Relative nitrogen concentration can be estimated from the refractive index as reported by Ruggles.\textsuperscript{17} We too have observed similar results in our nitrided oxides. The incorporation of nitrogen in the oxide leads to a change of structure from SiO\textsubscript{2} to Si–N–O. Meas et al.\textsuperscript{18} have observed that the refractive index of silicon nitride films increases with increase in nitrogen concentration, as determined from Auger electron spectroscopy measurements. We observed that refractive index of nitrided oxides increases with increase in nitridation time, temperature, and NH\textsubscript{3} content in the ambient. In an attempt to correlate the dependence of enhanced breakdown voltage with nitrogen concentration,
the breakdown field of various nitrided oxides versus their respective refractive indices is plotted in Fig. 8. It is seen clearly that with increase in refractive index of nitrided oxides the breakdown field also increases. This figure may be contrasted with Fig. 7. This suggests that the highest breakdown field of nitrided oxides is dependent on the amount of nitrogen incorporated into the oxide, which alters the structure of SiO₂. It is possible that during nitridation some of the weak spots or local defect sites which cause breakdown are reduced because of the incorporation of nitrogen. It is reported that in nitrided oxides the number of hole traps reduces with increase in nitridation conditions (nitridation time and temperature). Oxides having a large number of hole traps near the silicon interface are known to have low-field breakdown voltages. It is possible that during nitridation the incorporated nitrogen changes the structure and hence results in a smaller number of hole traps, increasing the breakdown field of nitrided oxides.

![FIG. 6](image_url)

![FIG. 7](image_url)

![FIG. 8](image_url)
Our results broadly indicate that the improvement in breakdown field is dominated by a change in the material structure of nitrided oxides (which possibly reduces the number of hole traps) rather than by electron traps. At the same time, we cannot rule out that electron traps do play some role in breakdown, since the results of $I-V$ and $I-t$ methods show that the current in nitrided oxides is less compared to dry oxides. Furthermore, it should be noted that breakdown may be altered by high local electron-trap densities in very small areas, whereas our measurements of electron traps (by $V_{FB}$ shifts) really gives the average over a large $1-mm^2$ area.

IV. CONCLUSIONS

Nitridation improves the breakdown strength of dry oxides, which is dependent on nitridation conditions such as time, temperature, and NH$_3$ content in the ambient. Our results show that the enhanced breakdown field of nitrided oxides is not due to the presence of the large number of electron traps, as no correlation between electron traps and breakdown voltage was observed. The higher breakdown field is dependent on the refractive index, which in turn is determined by the incorporation of nitrogen in the oxide which modifies the structure of nitrided oxides, possibly reducing the number of hole traps.

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