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Abstract

High quality silicon dioxide films have been produced using a direct plasma-enhanced chemical vapour deposition process with silane, nitrous oxide and helium that leaves a nitride layer at the Si-SiO_2 interface. X-ray photoelectron spectroscopy coupled with etch-back of the films has shown that the interface nitrogen is incorporated by nitridation of the silicon surface. Fowler-Nordheim injection measurements on thin films annealed after deposition for 1 minute at 950°C show that the neutral-trap generation and interface state generation rates are comparable to that of thermal oxide if a proper deposition power is chosen. Fast donor states, not P_b centres, account for almost all of the increase in the charge trapped at the interface. Too high deposition powers lead to excessive nitrogen and higher interface state generation rates. It is proposed that improved performance under hot-electron stress could be obtained by using an optimal deposition power to obtain an optimal nitrogen concentration followed by annealing in oxygen.

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I. INTRODUCTION

High quality oxides produced by low thermal budget processes have a number of important potential uses in the silicon-based electronics industry. Examples include thin-film transistors or solar cells on glass substrates, and Si-Ge metal-oxide-semiconductor field-effect transistors (MOSFETs)[1]. Oxide-nitride-oxide (ONO) stacked capacitor structures[2–4] are another instance where the conventional high temperature ($> 800^{o}$C) thermal oxide could be disadvantageous, especially if metal or silicide electrodes are to be substituted for polysilicon. Although thermal gate oxides will remain dominant in silicon based MOSFETs for the near future, as device dimensions shrink further, thermal budget issues will become an important issue even for this application.

It has been shown previously that oxides produced by plasma-enhanced chemical-vapour deposition (PECVD)[5–7] can have properties that approach those of thermal oxide and they can be used for making MOSFETs[8]. By carefully excluding oxygen or water vapour during the initial growth it has been shown[9] that nitrogen is incorporated at the silicon-silicon dioxide interface. This nitrogen may provide a potentially important advantage as a diffusion barrier against hydrogen[10], boron or other species[11,12]. Nitrogen is also believed to result in reduced susceptibility to hot-electron induced degradation[13,14] either through its action as a barrier to hydrogen which is involved in the degradation mechanism or by relieving the stress at the Si-SiO_2 interface[10,15]. It has been shown that there is an optimal amount of nitrogen in the near interface region that leads to an optimal decrease of the generation rate for interface states and this optimum is dependent on the process used to incorporate it[16].

The power used for the PECVD process and the temperature for the post-deposition annealing (POA) are key variables determining the quality of the oxide films. As power is increased the amount of nitrogen incorporated at the Si-SiO_2 interface increases[9]. At the same time the bulk properties of the oxide films more closely approach those of thermal oxide[17,18]. However, increasing the power may result in excessive nitrogen incorporation and increases the potential for damage created by ion bombardment[9]. Zhang *et al.*[19] have shown that the oxides produced by plasma processing have excess electron traps in addition to those that are related to the water, hydrogen and hydroxyl species originating with the hydrogen coming from the silane source. The high temperature processing characteristic of MOSFET fabrication or any explicit annealing steps reduces the concentration of traps[20,19] and can cause relaxation of the films.

In this paper we describe profiling of the nitrogen concentration in PECVD oxides as a function of RF power during deposition and as a function of post oxidation annealing conditions. The analysis was done using X-Ray photoelectron spectroscopy (XPS) coupled with etch-back of the oxide layer.

We also report on the effect of annealing and deposition power on the immunity of MOS capacitors made with these films to hot-electron induced degradation. Capacitance-voltage (CV) measurements were combined with Fowler-Nordheim (FN) injection to characterize the build up of charge in the films and the increase in interface state density D_{it} as a function of the electron fluence. We discuss the mechanism for interface state generation and speculate on ways of optimizing the performance of PECVD oxide films.

The paper is organized as follows: Section II describes the fabrication of the MOS capacitors, the analysis of the nitrogen profiles in the films by XPS, and the charge injection experiments. The results of the Fowler-Nordheim measurements are presented in Section III and discussed in Section IV. Conclusions follow in Section V.

II. EXPERIMENTAL

A. Film Deposition and XPS Analysis

The production of the PECVD films and their bulk properties have been described previously[9,18]. Briefly, silicon (100) wafers were given an RCA clean followed by an HF dip, water rinse, and blow dry with nitrogen immediately prior to deposition. N_2O-SiH_4-He mixtures with flows of 72, .18 and 960 sccm, respectively, were used in a commercial

13.56 MHz parallel-plate reactor at a pressure of 1.95 Torr and temperature of 390 ^oC. Care was taken to exclude both oxygen and water vapour from the system by enclosing it in a nitrogen-purged glove-box, resulting in oxides with an interfacial layer of containing nitrogen rather than the oxide characteristic of previous work[7].

XPS spectra were collected in a Perkin-Elmer PHI-5500 system with a monochromatic Al K_α source at a takeoff angle 75^o from the sample surface. Fig. 1 shows the XPS spectrum of a 3.5 nm film etched back from a 20 nm film deposited with 450 W of power. Two features at 398.0 and 402.6 eV can be attributed to nitrogen bonded to silicon and oxygen, respectively. Films were etched back in 1% HF solution and the concentration of N-Si and N-O bonds for films deposited at powers between 20 and 450 W is shown in Fig. 2. Note that the N-O bonds are found in the bulk of the film while, to within the resolution of the etch-back process, the N-Si bonds are found at the interface. The nitrogen concentration at the interface increases with increasing power and for the deposition done at 50 W amounts to about 4 atomic %. The concentration of N-O bonds in the bulk of the films also increases with power. It was found that annealing the films at 800^{o}C for 5 minutes or at 950^{o}C for 1 minute reduces the N-O bond concentration to below the detection limit of ≈ 0.1 atomic % while the concentration of N-Si bonds is unaffected.

To shed further light on the width of the nitride layer, the data of Fig. 2 were treated using the method of Vasquez *et al.*[21]. By using known electron mean free paths for the core levels and XPS data collected both before and after consecutive etch-backs, the method calculates the nitrogen atomic concentration within the layer that was removed by each etching step. The results shown in Fig. 3 indicate that most of the nitrogen lies within 1.0 nm of the silicon interface. This coupled with the fact that the nitrogen is bonded to silicon is consistent with the interpretation that the nitrogen is simply bonded to the silicon at the silicon-insulator interface as a result of a nitridation reaction that appears to dominate over deposition during the initial stages of film growth. If water-vapour or oxygen are not excluded from the chamber during these initial stages plasma oxidation rather than nitridation of the silicon dominates initially[7].

B. Electrical Measurements

Two sets of Fowler-Nordheim injection experiments were performed. For the first series 24 nm thick oxide films deposited at different power were subjected to annealing at different temperature to investigate the effect of power and annealing temperature on film properties. MOS diodes were formed by depositing 0.5 mm diameter Al gates through a shadow mask on films on 5 Ω-cm p-type silicon substrates. They were given a post-metal deposition anneal (PMA) for 15 minutes at 400^oC in forming gas (4% H_2 in nitrogen) prior to the formation of back contacts with InGa eutectic.

Measurements were done at constant current with an initial field of 7 MV/cm, while adjusting the applied gate potential to produce a current density of 10^{-6} A-cm^{-2}. Applied potentials were negative corresponding to electron injection from the gate. At intervals during the injection, quasistatic (QS) capacitance-voltage (CV) and high-frequency (100 kHz) capacitance-voltage characteristics were measured while scanning the gate potential from inversion to accumulation at a rate of 0.1 V/s. Interface state densities at midgap D_{itm} were obtained from the QS and 100 kHz CV data by the high-low method[22]. Bandbending potentials were calculated by integrating the quasistatic characteristic[23] referenced to the band-bending in accumulation. The flatband voltage was used to calculate the interface trapped charge by ignoring the charge trapped in the bulk of the film.

The second set of Fowler-Nordheim experiments involved injection at constant potential on samples with polysilicon gates. Films 9.5 nm thick were deposited on 5 Ω-cm n-type substrates which had a field oxide layer prepatterned with 2.25×10^{-4} cm^2 windows. These samples were annealed for 1 minute at 950^oC and top electrodes were deposited using a 630^oC *in-situ* n^+-doped polysilicon (poly) process and patterned by reactive ion etching. They were given a 20 minute PMA at 450^oC in forming gas following aluminum deposition for the back contacts.

In this case the measurements were done at constant positive voltages corresponding to electron injection from the substrate and the current change ΔJ across the capacitors was tracked along with the flatband voltage shift and interface state density. The expression given by DiMaria *et al.*[24] was used to convert the current change to a trapped charge density assuming the charge is trapped close to the Si-SiO_2 interface. In fact this method is not sensitive to charge trapped within a tunneling distance from the injecting interface[25].

III. RESULTS

A. Injection from Al gates

The trapped charge obtained from the flatband voltage shift and the midgap interface state density are shown in Figs. 4 and 5, respectively, as a function of injected charge fluence for 24 nm thick films. Data is shown for films deposited with 20 and 50 W of power and annealed in nitrogen for 1 minute at 950^{o}C or 10 minutes at 800^{o}C. In Fig. 4 there is an increase in negative trapped charge at intermediate fluences for the films annealed at the lower temperature. Apparently a significant number of traps responsible for this effect remain after annealing for 10 minutes at 800^{o}C but these are eliminated by annealing at 950^{o}C for 1 minute. This is consistent with previous results that have shown that high temperature annealing results in a reduction of the water-related and plasma-related traps[20,19].

At the highest fluences all the curves in Fig. 4 turn up indicating the creation of positive charge in the films. This could be related to the creation of anomalous positive charge (slow states)[26,27], or hole traps near the interface[24,28]. The rate of increase in flatband voltage for the highest fluences is reduced in Fig. 4 for higher power or higher annealing temperature with the increase in interface state density shown in Fig. 5 showing a similar trend. To investigate the origin of the trapped charge and interface states further investigations were focused on the higher deposition powers of 50 or 450 W and the higher annealing temperature of 950^{o}C. Poly gates were used to minimize the effect of hydrogen released by the interaction of water species with the gate[29].

B. Injection from Silicon Substrate - Poly Gates

Figs. 6, 7, and 8 show results obtained on poly capacitors for films 9.5 nm thick deposited using 50 W of power and annealed for 1 minute at 950^{o}C. Fig. 6 shows the 100 kHz CV curves as a function of fluence for a constant pulsed voltage corresponding to an initial applied field of 13.2 MV/cm. Figure 7 shows the interface state densities as a function of energy above the valence band edge obtained by the high-low method. In this case data are shown for zero fluence and a fluence of 0.18 C/cm^2 obtained with an applied field of 8.4 MV/cm.

Charge densities obtained from flatband voltage shifts ΔV_{fb} and current changes ΔJ are shown as a function of fluence in Fig. 8 along with the increase in the midgap interface state densities ΔD_{itm}. Data are shown for 9.5 nm thick films for applied potentials of 8.0 and 12.5 V, corresponding to initial fields of approximately 8.4 and 13.2 MV/cm and initial current densities of approximately 2×10^{-4} and 10 A/cm^2, respectively.

Finally, the effect of using 450 W of deposition power to produce 13.5 nm thick films is shown in Fig. 9 where ΔD_{itm} is plotted as a function of fluence for constant pulsed voltages corresponding to initial applied fields of 7.1 and 10 MV/cm. These films were also given a 1 minute POA at 950^{o}C.

IV. DISCUSSION

Two general statements can be made about the interface states generated during by the Fowler-Nordheim injection on all the poly-gated samples. Firstly, from the marked position of the flatband capacitance C_{fb} in Fig. 6 it can be seen that the interface states are donors from the valence band maximum to a point very close to the conduction band edge. In fact if it is assumed that above this point the interface states are acceptors, then interface states can account for all of the flatband voltage shift. However, as shown below we observe electron trapping near, but not at the interface that could also account for the negative shifts in the CV curves near the conduction band-edge.

The second point is evident from the data of Figure 7 where the interface state density is shown for two fluences obtained with an initial applied field of 8.4 MV/cm. At the higher fluence of 0.18 C/cm^2 D_{it} is relatively flat as a function of energy above the valence band maximum from flatbands to inversion, the range over which the high-low method is relatively accurate. The P_b centre is amphoteric and has a donor state at an energy $E_v + 0.30$ eV and an acceptor state at $E_v + 0.80$ eV[30]. These characteristics peaks are not seen in Fig. 7 or in any of our higher fluence data. This is not conclusive evidence; however, when coupled with the fact that the interface states appear to be donors over most of the bandgap the data suggest that most of the generation mechanism is not related to the P_b centre.

Referring specifically to the 8.4 MV/cm data for the 9.5 nm films of Fig. 8a, at high fluence the charge calculated from ΔJ is positive and saturates at a relatively small value which may be due to hole trapping[28] or anomalous positive charge[24]. The density of interface states at a fluence of 0.1 C/cm^2 measured here (4×10^{11} eV^{-1}cm^{-2}) is about a factor of 2 higher than that for the 9.3 nm thick thermal oxides measured for a field of 9.0 MV/cm (2×10^{11} eV^{-1}cm^{-2}) shown in Fig. 15 of Ref. 24 but less than the level (6×10^{11} eV^{-1}cm^{-2}) reported by Krisch *et al.*.[15] for thermal oxides under similar conditions.

At the higher field of Fig. 8b the generation rate for interface states is higher and, as shown by the sloped lines in Fig. 8, the functional dependence of ΔD_{itm} goes from sub-linear at 8.4 MV/cm to roughly linear at 13.2 MV/cm. At the higher field the charge determined from ΔJ is negative. This is partly due to an increased generation rate of neutral electron traps and the fact that the tunneling distance moves closer to the interface with higher applied potential. For 9.5 nm thick films this distance is on the order of 3.7 and 2.4 nm, respectively for applied potentials of 8.0 and 12.5 volts.

The density of electron traps N_t and their cross-section σ can be related to the charge N_n deduced from the ΔJ data of Fig. 8b by using the simple relationship,

$$N_n = N_t[1 - \exp(-F\sigma/e)], \tag{1}$$

where e is the electron charge and F is the fluence. By using the method of DiMaria and Stasiak[20] we find $\sigma = 4 \times 10^{-19}$ cm^2, close to the value obtained for thermal oxides in Ref. 20. We also find an initial trapping probability $N_t\sigma = 2 \times 10^{-7}$ which is small considering the high field of 13.2 MV/cm. By comparison Fig. 10 of Ref. 24 shows a comparable initial trapping probability for injection into a 9.3 nm thick thermal oxide using a field of 9.0 MV/cm. This analysis does not include the effect of detrapping at these high fields[24].

At very high deposition powers corresponding to high levels of nitrogen at the interface, the interface state generation rate increases dramatically, as shown in Fig. 9. The functional dependence on fluence is linear for both fields (7.1 and 10 MV/cm). Increased interface state generation rates have been observed for oxides lightly nitrided in ammonia[15] which are greatly reduced after reoxidation. This indicates that a reoxidation or an initial annealing in oxygen instead of nitrogen could improve the performance of our oxides.

The concentration of nitrogen near the Si/SiO_2 interface observed in Fig. 2 for a deposition power of 50 W is close to the 5 at.% level reported previously[14,15]. Dutoit *et al.*[16] have shown that there is an optimum level of nitrogen at the interface which depends on the method used to introduce the nitrogen. The levels they quote as an optimum (0.5-2 at.%) indicate that we might observe improvements by going to lower deposition powers. However, their concentrations are lower than those quoted by other authors[14,15] and this may indicate a different resolution for their Auger depth-profiling technique.

A generation rate for fast states which increases with field and an increase of electron trap generation with field are characteristic of traps generated by hot electrons. This has been shown[20] to involve the generation of a mobile hydrogen-related species near the anode which creates fast states at the Si-SiO_2 interface and electron traps close to it. Two mechanisms have been proposed to account for the interface state generation. The first involves the depassivation of P_b centres by the released hydrogen[29,31] and the second involves strained Si-O bonds near the interface which trap holes that recombine with injected electrons to form the interface states[32]. As noted above, we see no strong sign of P_b centers in our D_{it} data which argues against a depassivation mechanism involving this defect.

Cartier *et al.*[33] have shown that P_b centres account for only a small amount of the interface states produced by atomic hydrogen. More recent work at Delft[34,35] has shown that fast donor states are created by the recombination of electrons with trapped holes (generated by vacuum ultraviolet radiation) near the interface and that this process is induced by hydrogen. The generation of interface states in PECVD oxides may be related to this mechanism since holes could be injected from the anode for these films[24]. The increase of the interface state generation rates observed for the films deposited with 450 W of power may be related to one of two consequences of increased power, increased incorporation of nitrogen in the films or increased damage of the silicon substrate.

Finally, the results seem to indicate that the nitride is too close to the interface to act as an effective hydrogen barrier.

V. CONCLUSIONS

Nitrogen can be incorporated near the interface of PECVD oxides deposited in a parallel-plate reactor by using nitrous oxide as the oxidant and ensuring that no oxygen or water vapour are present in the chamber during the initial stages of deposition. XPS analysis coupled with etch-back of the films indicates that the nitrogen is bound to silicon at the silicon surface. The amount of nitrogen at the interface is a function of power used during the deposition.

CV analysis performed at intervals during Fowler-Nordheim injection into the films indicates that the amount of electron trapping and the interface state generation rate in the films decreases with increasing deposition power and annealing temperature. By depositing with 50 W of power and annealing for 1 minute at 950°C, 9.5 nm thick films have been obtained that have about 5 at.% nitrogen at the interface and have interface state generation rates and electron trap generation rates that are comparable to those of the best thermal oxides.

The generated interface states are fast donor states that do not exhibit the density variation with bandbending characteristic of P_b centres. This indicates that they may be created by the neutralization of trapped holes created by anode hole injection.

Too high a deposition power degrades the interface by incorporating excessive nitrogen at the interface and possibly by creating too much ion-bombardment damage. By varying the deposition power to optimize the nitrogen concentration and by annealing in oxygen rather than nitrogen it may be possible to improve the hot-electron immunity of PECVD oxides to the levels obtained for reoxidized-nitrided oxide films.

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FIGURES

FIG. 1. Photoelectron spectrum of a 3.5 nm film etched back from a 20 nm film deposited with 450 W of plasma power.

FIG. 2. Concentration of N-Si and N-O bonds as a function of etched-back thickness for films deposited at four levels of RF power.

FIG. 3. Data of 450 W films of Fig. 2 corrected using method of Ref. 21

FIG. 4. Charge determined from flatband voltage shift as a function of fluence of electrons injected from an Al electrode into 24 nm thick films deposited at 20 and 50 W of power on *p*-Si substrates. Films were annealed in nitrogen for 10 minutes at 800 ^{o}C or for 1 minute at 950 ^{o}C.

FIG. 5. Midgap interface state density as a function of injected fluence for samples of Fig. 4

FIG. 6. 100 kHz CV characteristics for fluences between 0 and 0.7 C/cm^2 obtained using an initial applied field of 13.2 MV/cm on a 9.5 nm thick film deposited with 50 W of power and annealed for 1 minute at 950^{o}C. Electrons were injected from the *n*-Si substrate using a constant pulsed voltage

FIG. 7. Interface state density as a function of energy above the valence band edge obtained at zero fluence and a fluence 0.18 C/cm^2 for the same film as Fig. 6. Electrons were injected from the *n*-Si substrate using a constant pulsed voltage corresponding to an initial applied field of 8.4 MV/cm.

FIG. 8. Charge determined from flatband voltage shift and current variation and midgap interface state density as a function of fluence. The 9.5 nm thick films were deposited with 50 W of power and annealed in nitrogen for 1 minute at 950 ^{o}C. For (a) electrons were injected from the *n*-Si substrate using a constant pulsed voltage corresponding to an initial applied field of 8.0 MV/cm. and for (b) the constant pulsed voltage was 12.5 V for an initial field of 13.2 MV/cm.

FIG. 9. Midgap interface state density as a function of injected fluence for 13.5 nm thick sample deposited with 450 W of power and annealed for 1 minute at 950°C. Electrons were injected from the n-Si substrate using constant pulsed voltages corresponding to initial applied fields of 10.0 and 7.1 MV/cm.