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Oxidation of silicon nitride films in an oxygen plasma

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The fabrication of oxynitrides using low thermal budget process technology is a key component in the production of advanced devices. This work focuses on the use of plasma anodization of low-pressure chemical vapor deposition (LPCVD) silicon nitride films to produce silicon oxynitride films, which are characterized structurally and electrically. The oxynitride dielectric films have a three layer structure, with “SiO₂”-like layers at the surface and near the interface, and a “Si₃N₄”-like layer between them. Hence, nitrogen atoms are replaced by oxygen atoms at the surface of the film and near the Si/dielectric interface. The conductivity of the silicon nitride film was found to be higher than the silicon oxynitride film, whereas the conductivity of the oxynitride and, therefore, its trapping characteristics are more temperature dependent. Furthermore, the activation energy required to release an electron from a trap in the silicon oxynitride film (0.218 eV) is $1.7\times$ that of the silicon nitride film (0.130 eV). Although oxidation of the LPCVD silicon nitride film did not reduce the interface trap density ($\approx 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ for both Si₃N₄ and SiON films), the density of traps, which are thought to be silicon dangling bonds in the form of an sp^3 state near midgap, have reduced. A model to explain the conduction properties of the silicon oxynitride film—based on the Fowler–Nordheim conduction mechanism—was developed. Moreover, this model takes into account the trapping dynamics of the film. It was found that the best theoretical fit to the experimental current density data was obtained by assuming that the areal trap density, $N_o = 5 \times 10^{12} \text{ cm}^{-2}$ and the trap capture cross section, $\sigma = 1 \times 10^{-16} \text{ cm}^2$. © 1999 American Institute of Physics. [S0021-8979(99)01105-6]

I. INTRODUCTION

Fabrication of transistors for advanced microchips requires novel processing strategies which allow considerable reduction in device dimension size. The nature of such strategies involves the use of low thermal budget¹ processes in order to maintain the structural integrity of the device while minimizing the number of defects produced by the process technology.²

For this purpose plasma grown low temperature silicon dioxide layers represent a good alternative to thermally grown layers. It has been shown that, following plasma oxidation, dopant redistribution is negligible³ and the “bird’s beak” structure, produced during thermal oxidation, is minimized.⁴ One of the main advantages of plasma grown layers is that silicon is consumed during the process, by contrast with layer deposition, thereby replicating at lower process temperatures the thermal Si/SiO₂ system.⁵ Plasma grown oxides on single crystal silicon have produced interface states below $10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ measured using the G_p/ω technique,⁶ and with mean dielectric breakdown strengths in excess of 10 MV cm^{-1} for an oxide thickness of $<50 \text{ nm}$.⁷ Furthermore, previous work also shows that good quality plasma grown oxides on SiGe, SiC, polycrystalline and amorphous silicon have been demonstrated.^{8–10}

An investigation of the plasma oxidation of silicon nitride has been undertaken since it has been reported that an

oxynitride dielectric exhibits certain advantageous electrical properties compared with an oxide. These properties are higher dielectric breakdown values and reliability,^{11–13} reduced interface state generation¹⁴ and improved I - V and C - V characteristics.¹⁵ Initially, work on the plasma anodization of silicon nitride was undertaken in order to establish the feasibility of using Si₃N₄ as a mask against oxidation.⁴ It was found that when strips of Si₃N₄ were used as a mask against oxidation the Si₃N₄ was gradually converted to SiO₂. This conversion is thought to be due to a loss of nitrogen into the plasma caused by bonding instability of nitrogen at the surface of the dielectric.¹⁶ In further work by Goswami *et al.*,¹⁷ Si₃N₄ films were deposited on silicon by plasma enhanced chemical vapor deposition (PECVD) using a SiH₄/NH₃ plasma at 300 °C. The Si₃N₄ films were then anodized in an oxygen plasma with a sample temperature of 400 °C. This produced an oxynitride dielectric which was reported to have a lower fixed oxide charge, leakage current and interface trap density than the original PECVD nitride. Fourier-transform infrared (FTIR) data showed the gradual transformation of the nitride into an oxynitride structure. Kennedy *et al.*¹⁸ continued this work further through the plasma oxidation of LPCVD Si₃N₄ films in a plasma anodization reactor.⁶ This work showed that a PMA treatment after oxidation of the silicon nitride film can significantly reduce the interface trap density of the resulting silicon oxynitride film. Also, a mechanism of conduction in silicon oxynitride films was proposed based on electron tunneling to and subsequent re-emission of electrons from shallow traps in the dielectric to

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the oxynitride conduction band following the work of Yang *et al.*¹⁹

A recent literature search has shown that little work has been done on the oxidation of Si_3N_4 films to produce silicon oxynitrides. Lukovsky *et al.*²⁰ presented work on the integration of plasma assisted and rapid thermal processing to produce low thermal budget ultrathin dielectrics. Kaluri *et al.*^{21,22} presented the most recent method of producing oxynitrides using plasma anodization involving the use of an N_2O plasma to anodize silicon. Their optimum growth conditions for silicon oxynitrides were 400 °C, 15 mTorr, 25 sccm and a constant current of 3.8 mA cm⁻². Under these conditions, it was found that no nitrogen was detected in the bulk region of the film, however, it was detected within 4.5 nm of the interface in the form of N-Si₃ bonding structures. The oxide charge density and the breakdown field strength were found to be 1.1×10^{11} cm⁻² and 8.4 MV cm⁻¹, respectively.

The advantage of plasma anodization of silicon nitride in an oxygen plasma is that an oxynitride can be produced by a low thermal budget process. The aim of our work was to investigate further the physical and electrical properties of the plasma oxidized Si_3N_4 films. For this purpose we used Auger electron spectroscopy (AES) and FTIR spectroscopy for physical characterization. The resultant physical data were then correlated with the data from the electrical characterization measurements. The electrical characteristics were measured using quasistatic *C-V* and *I-V* measurements of metal-insulator-semiconductor (MIS) capacitors formed using silicon nitride and silicon oxynitride dielectric films. The *C-V* measurements were used to assess the trap distribution in the silicon band gap, while the *I-V* measurements were used to assess the breakdown and conduction properties of the silicon nitride and oxynitride films. Furthermore, an improved model of conduction in silicon oxynitride films produced by plasma anodization is presented.

II. EXPERIMENT

A. Plasma anodization

The silicon nitride films were plasma anodized in an oxygen plasma in an inverted plasma anodization system.⁶ The basic principle of the system is to expose a silicon substrate to an oxygen plasma generated by rf induction coils located around the process tube at a distance of 6 cm from the substrate. Throughout the growth process a dc electric field is applied across the plasma using the substrate and another silicon wafer as electrodes; the growth substrate is connected to ground while the lower silicon wafer acts as a cathode. As a result of this electric field, negatively charged oxygen species drift towards the substrate and some react with the silicon nitride film at the surface while some migrate through it and react with the underlying silicon.

The process chamber of the inverted plasma oxidation system consists of a quartz tube of approximately 5 in. in diameter and 3 mm thick. A quartz ledge is located above the position of the plasma where a quartz mask and the growth substrate sit throughout the process. The mask is used to isolate the grounded stainless steel anode, which rests against

the back of the growth wafer, from the plasma. Usually a blank substrate is placed between the substrate and the anode to prevent any possible ionic contamination from the anode reaching the back of the substrate.

A rotary pump is used to keep the process chamber under reduced pressure and a Baratron pressure gauge is used to monitor the pressure in the chamber. Mass flow controllers are used to allow a flow of filtered semiconductor grade oxygen into the chamber and to maintain a pressure of 0.15 Torr during processing. A Millipore filter is also used to maintain the purity of the gas flowing into the process chamber.

The substrates used in this investigation were 5 in. (100) RCA cleaned silicon wafers which were boron doped to 5×10^{14} cm⁻³. LPCVD Si_3N_4 films were then deposited to a thickness of 20 nm at 780 °C. The plasma oxidation reactor described above was used to anodize the Si_3N_4 films at constant voltage in an oxygen plasma under the following process conditions: an rf power of 0.6 kW, a dc bias of 150 V, a process pressure of 150 mTorr and a process temperature of 430 °C, respectively. Only the central area of the Si_3N_4 film of diameter 6.9 cm was exposed to the oxygen plasma for times ranging from 10 to 30 min. Following plasma anodization, an array of MIS capacitors was formed by the evaporation of 200 nm of high purity aluminium through a shadow mask which was placed so as to form MIS capacitors on both the oxidized Si_3N_4 portion of the substrate as well as the Si_3N_4 portion. The nitride layer on the back of each sample was removed using emery cloth and an ohmic contact was formed by Al evaporation. Each of the processed substrates was cut in half; one half received a PMA treatment in forming gas (90% N_2 /10% H_2) for 30 min at 400 °C and the other half was left "as grown."

B. Structural measurement

An Escalab II Auger electron spectrometer was used to detect oxygen and nitrogen in the LPCVD nitride and plasma oxidized Si_3N_4 samples. An area of 1 cm² of both samples was loaded into the high vacuum chamber of the spectrometer in turn. They were then examined by scanning an electron beam across the surface of the sample to release an Auger electron. In the Auger electron spectrum the number of Auger electrons emitted by the dielectric is plotted as a function of energy in eV, thus enabling constituent elements to be identified. Each scan was followed by ion beam milling to remove some dielectric material from the surface of the sample. Hence, Auger spectra of the constituent elements of the dielectric were measured with depth through the dielectric film.

A silicon wafer, having similar properties to those of the deposited film substrates, was used as a reference sample for the FTIR measurement. The analysis of the starting material (the Si_3N_4 film) and the lightly oxidized Si_3N_4 dielectric layer was done by transmission infrared spectroscopy in the 400–1200 cm⁻¹ range, using a dual beam spectrometer.

C. Electrical measurement

The MIS capacitors were probed in a grounded metal enclosure and gate-substrate I - V characteristics were obtained using a Keithley voltage source (type 230) and electrometer (type 617) using an automated arrangement driven by a PC. A bias was applied to the MIS capacitor and the resultant current flowing through it was measured after a given settling time. Experimentally it was found that the system was capable of measuring currents accurately down to 1×10^{-12} A. Below this value the recorded data were unreliable due to unwanted leakage currents.

The breakdown field strength of each dielectric film was determined by applying a ramp voltage of -2 V s^{-1} to the gate of the MIS capacitor under test. The bias at which a current of $1 \mu\text{A}$ flowed through the capacitor was defined to be the breakdown field strength. A breakdown histogram composed of the breakdown field strengths of 20 capacitors from each dielectric film was produced. These data were then used to plot a cumulative breakdown field distribution from the silicon nitride and silicon oxynitride films.

The low frequency capacitance voltage (C - V) measurement technique was developed by Kuhn²³ and is known as the quasistatic technique. In this method a slow voltage ramp is applied to the gate of the MIS capacitor and the resultant displacement current is measured using an electrometer. The interface trap density at the silicon-dielectric interface was determined by comparing the experimental C - V curve with a theoretical one generated by fitting it to the experimental one in accumulation.

III. RESULTS

A. Structural properties

Taylor *et al.*⁴ examined the effect of plasma anodization of Si_3N_4 in an oxygen plasma. After a 3 h oxidation $0.45 \mu\text{m}$ of plasma oxide was grown on a patterned silicon substrate with $\text{Si}_3\text{N}_4/\text{SiO}_2$ strips. This corresponds to an oxide growth rate¹⁶ of 0.038 nm s^{-1} , assuming constant current conditions. As a result of this, approximately $0.06 \mu\text{m}$ of Si_3N_4 was consumed vertically. Therefore, the rate of conversion of Si_3N_4 to SiO_2 is $5.1 \times 10^{-3} \text{ nm s}^{-1}$. This conversion of Si_3N_4 to SiO_2 is probably due to a loss of nitrogen into the plasma caused by bonding instability of nitrogen at the surface of the dielectric and at the same time oxygen replaces nitrogen at the surface of the dielectric. A similar suggestion was also made by Kaluri *et al.*^{21,22} who presented a description of nitrogen incorporation in thin silicon oxides using a N_2O plasma to anodize silicon. They suggested that negative nitrogen moieties, perhaps N_2^- , NO^- , etc., were formed on the silicon surface upon collision with an electron drift through the oxide towards the positively biased silicon, and react to form Si_3N_4 . Hence, nitrogen in the $\text{N}-\text{Si}_3$ (397.7 eV) bonding arrangement is formed primarily at the $\text{Si}-\text{SiO}_2$ interfacial region, and the concentration of nitrogen in the $\text{Si}-\text{SiO}_2$ interfacial region increases with oxidation time. Therefore, as the $\text{N}-\text{Si}_3$ front moves away from the interface during oxidation, bonding stability is lost, resulting in the formation of molecular nitrogen which subsequently exits the oxide in the formation of silicon oxynitride bonding structures.

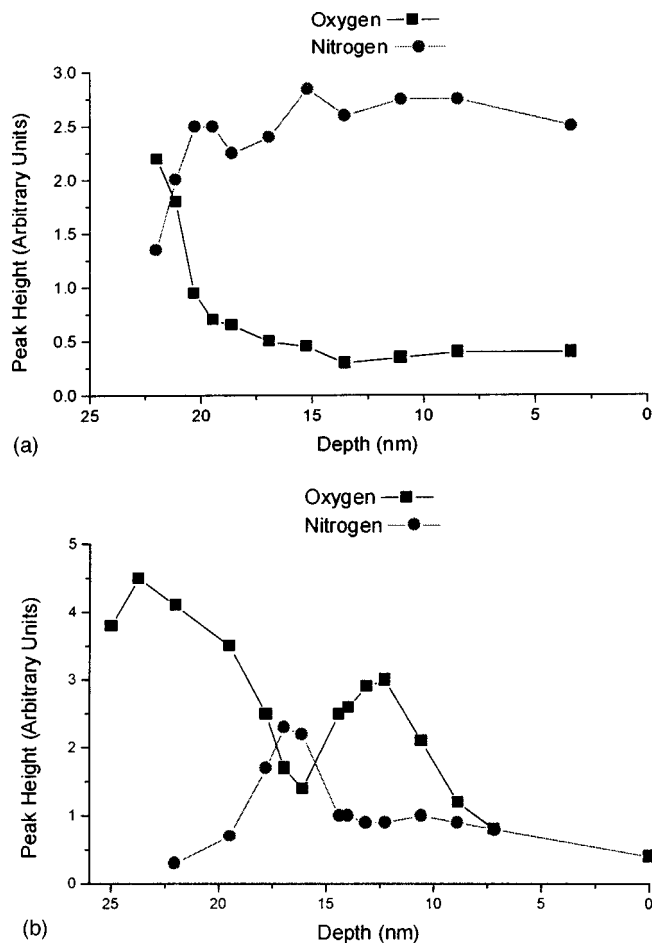


FIG. 1. Depth profiles showing the nitrogen and oxygen composition of the (a) 21 nm silicon nitride, and (b) 25 nm silicon oxynitride films. These data were obtained by Auger electron spectroscopy.

Auger depth profiles of the 20 nm LPCVD silicon nitride sample and the oxidized silicon nitride (oxynitride) sample are shown in Figs. 1(a) and 1(b), respectively. Clearly there is a distinct difference in the structural nature of both of these samples. The nitride sample is composed primarily of nitrogen with a small but significant amount of oxygen at the surface of the film. However, the oxynitride appears to be a three layer structure composed of oxygen rich layers at the surface and near the interface with a nitrogen rich layer sandwiched between them. Hence the effect of plasma anodization has been to replace the nitrogen near the interface and at the surface by oxygen.

Analysis of the Auger spectra for the lightly oxidized Si_3N_4 film revealed the carbon 1s, nitrogen 1s, oxygen 1s, and silicon 2p lines. However, the carbon 1s peak (C 1s) was recorded only in the Auger spectra of the surface of the sample. This is probably due to the adsorption of contaminants on the surface of the silicon nitride film aided by its porosity.

There were two nitrogen 1s peaks which were recorded in the depth profile of the lightly oxidized Si_3N_4 film. The first one (N-I) is located at 394 eV and the second one (N-II) at 400 eV. The existence of the two lines is suggesting that both $\text{Si}_2=\text{N}-\text{O}$ and $\text{Si}\equiv\text{N}$ bonds are present in the sample. No nitrogen was detected on the surface of the initial sample,

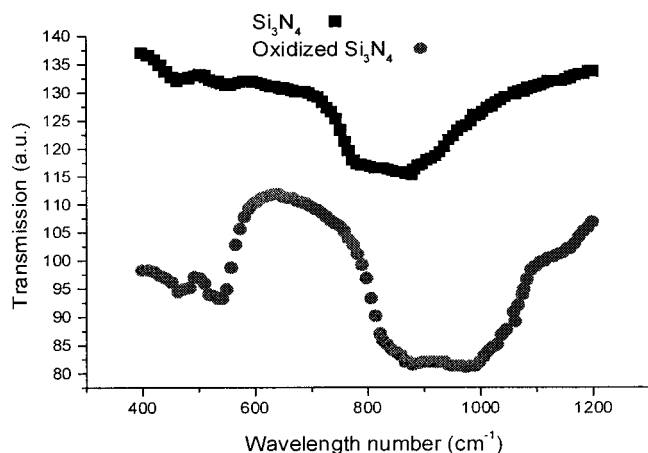


FIG. 2. FTIR spectra of the 21 nm silicon nitride and the 25 nm silicon oxynitride films.

however, as the sample was probed deeper the nitrogen concentration reached a maximum. The majority of nitrogen atoms at this depth were of the form “Si≡N.”

The oxygen O 1s peak was detected in all three regions of the sample (i.e., surface, middle, and interface). At the surface the oxygen line consists of two different lines, which we believe represent: (i) oxygen in the silicon suboxides (524.5 eV), and (ii) adsorbed oxygen (533.1 eV). Moreover, the existence of some oxygen in the structure of the starting material (i.e., Si₃N₄) was confirmed by measurements using spectroscopic ellipsometry. However, its refractive index at the mercury green line (546 nm) is 1.79, which is very low as compared with other results²⁴ which are in the 1.98–2.20 range. This effect could be due either to the presence of some oxygen in the structure or perhaps the silicon nitride structure could be slightly porous (for example, due to a low deposition temperature).

From the FTIR spectrum of the silicon nitride film there is a broad adsorption centered around 880 cm⁻¹ (Fig. 2). The broadness of this absorption is due to the fact that there are several contributions to this line: (i) Si–N bonds (stretching vibration at ≈840 cm⁻¹), and (ii) Si–O bonds (stretching and conformation vibrations, usually at 1090 and 810 cm⁻¹, respectively). Also the Si–O bending vibration was recorded at 465 cm⁻¹. Hence, the presence of the oxygen related vibrations in the IR spectra of the Si₃N₄ spectra is clearly showing that the oxygen content is high enough to affect the structure of the initial film.

For the lightly oxidized silicon nitride film, the spectra features belonging to the oxygen bonds are more accentuated (Fig. 2). The most important change is the one related to the Si–O stretching vibration which is more prominent and is, therefore, affecting the structure of the band related to Si–N stretching vibrations.

B. Bulk electrical properties

Cumulative breakdown field distributions of breakdown histogram data from the as deposited silicon nitride and the as grown silicon oxynitride films were plotted in Fig. 3. These distributions show that the breakdown field strengths

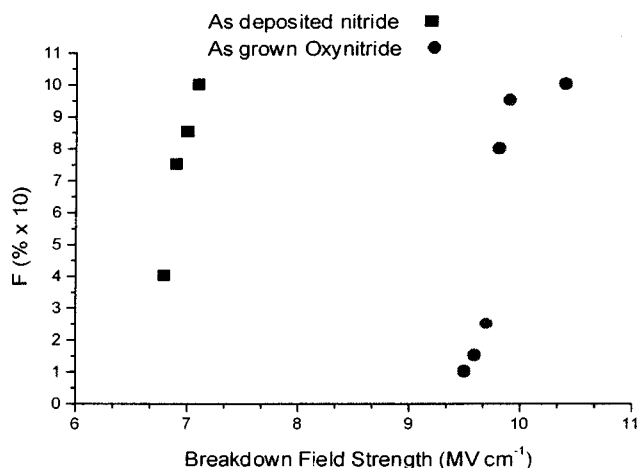


FIG. 3. Cumulative breakdown distribution showing the percentage of dielectric breakdowns at a given breakdown field strength from a sample of 20 MIS capacitors with silicon nitride and silicon oxynitride dielectric films.

of each film were reasonably uniform. Furthermore, the breakdown field strength is shown to improve by over 2 MV/cm through the oxidation of the as deposited silicon nitride film producing the as grown silicon oxynitride film.

Poole–Frenkel (or bulk limited conduction) occurs when the conductivity of the dielectric film is dependent on the electric field, E . This process is thought to originate from field enhanced thermionic emission from defects in the bulk of the dielectric. In his theoretical analysis, Frenkel²⁵ assumes that each defect is charged and represents a fixed Coulombic potential. When an electric field is applied, the potential surrounding the trap becomes a superposition of the trap and the potential resulting from the applied field. As a consequence of the applied field the barrier height, ϕ_1 , to thermionic emission is reduced. Hence, when an electric field is applied across the dielectric, electrons or holes hop from trap to trap under the influence of the applied field. The equation which describes the Poole–Frenkel conduction mechanism is described below in the form of the Poole–Frenkel current density, J_{PF} :²⁶

$$J_{PF} = C_{PF} E \exp \left\{ \frac{-q}{kT} \left(\phi_1 - \sqrt{\frac{qE}{\pi \epsilon_0 \epsilon_{rd}}} \right) \right\}, \quad (1)$$

where C_{PF} is the Poole–Frenkel proportionality constant (related to defect density), q is the electronic charge, k is Boltzmann’s constant, T is the absolute temperature at which the measurement was performed, ϵ_0 is the permittivity of free space and ϵ_{rd} is the dynamic dielectric constant.

Fowler–Nordheim (or electrode limited) conduction^{27,28} occurs as a result of electrons tunneling from a metal or semiconductor surface through the energy gap of the dielectric into the conduction band of the material at the other side of the dielectric. Electrons incident on the dielectric at the Fermi level experience a potential barrier, ϕ_0 . According to classical mechanics, any electron incident on the potential barrier is reflected and for an ideal insulator conduction can only occur if the electrons in the metal or semiconductor gain sufficient thermal energy to overcome the potential barrier, or, in other words, by thermionic emission. However, as

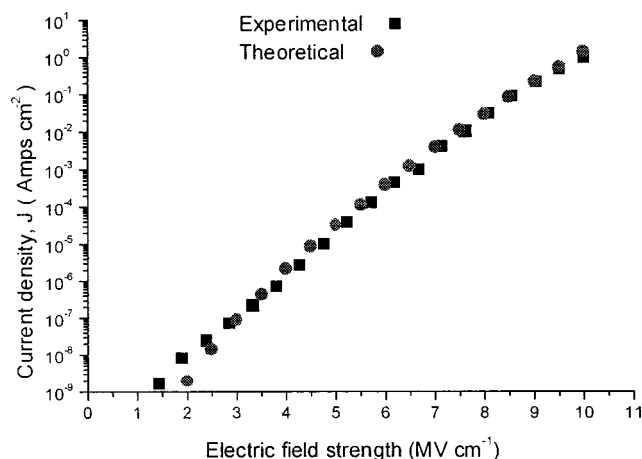


FIG. 4. J - E plot of the experimental current density calculated from the measured I - V data of a silicon nitride MIS capacitor. A theoretical Poole-Frenkel J - E curve is found to be coincident with the experimental data. The Poole-Frenkel proportionality constant, the dynamic dielectric constant, and the barrier height of defects within the film were calculated to be 1.52×10^{-6} , 7.74 and 0.809 eV, respectively.

a consequence of quantum mechanics these electrons have a finite probability of transmission into the energy gap of the dielectric. Therefore, when a large electric field is present in the insulator, this results in the flow of an appreciable current. The current density, J_{FN} , is related to the field in the dielectric by

$$J_{FN} = C_{FN} E^2 \exp\left(\frac{-\beta}{E}\right), \quad (2)$$

where the pre-exponential constant is given by

$$C_{FN} = \frac{q^3 m_o}{16\pi^2 \hbar m_{ox} \varphi_o} \quad (3)$$

and the exponential term, β is

$$\beta = \frac{4}{3} \sqrt{\frac{2m_{ox}}{q\hbar}} \sqrt{\varphi_o^3}, \quad (4)$$

where E is the electric field across the dielectric, q is the electronic charge, m_o and m_{ox} are the electron rest mass and the effective mass of the electron in the dielectric, respectively, and $\hbar$ is the reduced Planck's constant (i.e., $h/2\pi$).

The experimental J - E characteristics of the LPCVD silicon nitride film are presented in Fig. 4. These characteristics were calculated from the I - V raw data using the relations $E = V/d$ and $J = I/A$ where d is the thickness of the dielectric and A is the area of the MIS capacitor. The current density passing through the dielectric increases exponentially between field strengths of 0.5 and 10 MV cm^{-1} and was found to be polarity independent. Over most of the range of field strength, $>2 \text{ MV cm}^{-1}$, the gradient of the data is almost constant. By replotting in the form of a Poole-Frenkel plot (J/E vs $\sqrt{E}$), it was possible to calculate the dynamic dielectric constant from the slope of the best straight line fit through the data. The barrier height of defects within the film was calculated from the intercept on the J/E axis. For the as

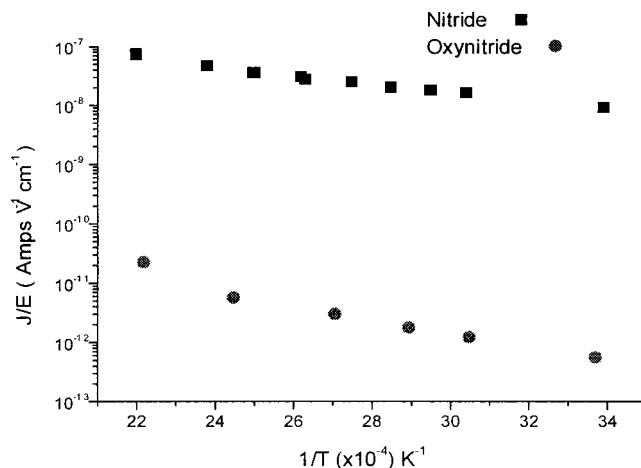


FIG. 5. Arrhenius plot (J/E vs $1/T$) over the temperature range of 21–227 °C for the silicon nitride and silicon oxynitride MIS capacitors.

deposited Si_3N_4 film the dynamic dielectric constant and the barrier height of defects within the film were calculated to be 7.74 and 0.809 eV, respectively.

The temperature dependence of conductivity in the silicon nitride and oxynitride dielectrics is presented in the Arrhenius plot (J/E vs $1/T$) over the temperature range of 21–227 °C (Fig. 5). The conductivity of the silicon nitride film is at least three orders of magnitude greater than the silicon oxynitride film. This plot is also representative of the temperature dependence of trapping within each of these films. The activation energy, which is the amount of energy required to release an electron from a trap with a Coulombic potential barrier, was determined from the slope of the plot. Hence, for the nitride and oxynitride dielectrics, this was found to be 0.130 and 0.218 eV, respectively. Therefore, almost double the amount of energy is required to release an electron from a trap in the oxynitride by comparison with the nitride. Furthermore, the proportionality constant associated with the Poole-Frenkel conduction equation was found to be 1.52×10^{-6} from the point where the data crosses the J/E axis for $(1/T) \rightarrow \infty$.

The experimental J - E characteristics of the silicon oxynitride dielectric are presented in Fig. 6. In contrast to the silicon nitride case, the I - V data were found to be polarity dependent, which is evidence of an electrode limited conduction mechanism. For electron injection from the metal (silicon positively biased), the current density passing through the dielectric remains below $10^{-8} \text{ A cm}^{-2}$ until approximately 4.9 MV cm^{-1} . At this point the current density increases exponentially with a constant gradient until it reaches a value between 10^{-6} and $10^{-5} \text{ A cm}^{-2}$. Here the rate of change of current density with electric field strength reduces, which we attribute to be due to electron trapping in the oxynitride film. It is well known that a buildup in trapped negative charge in a dielectric film inhibits the injection of further electrons.²⁹ This effectively decreases the electric field strength at the cathode, reducing the current density until all of the traps are in equilibrium (dynamic balance) with the current flow. This may be modeled as shown below.

When an electric field was applied across the oxynitride

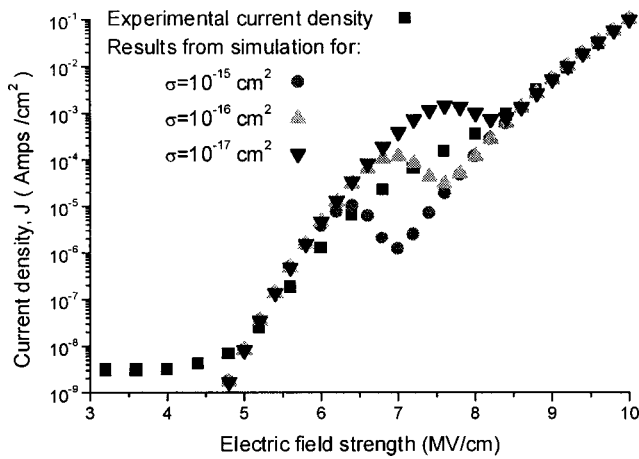


FIG. 6. J - E plot of the experimental current density calculated from the measured I - V data of a silicon oxynitride MIS capacitor. A theoretical Fowler–Nordheim J - E curve modified to account for a dynamic trapping process in the oxynitride shows a reasonable fit to the experimental data. The barrier height to electron emission, the areal density of traps and the trap capture cross section are 2.4 eV, $5 \times 10^{12} \text{ cm}^{-2}$ and $1 \times 10^{-16} \text{ cm}^2$, respectively.

dielectric such that electrons were injected into it from the metal, the electrons experienced a potential barrier of 2.4 eV. This barrier height was calculated by assuming that the theoretical current density curve, based on the Fowler–Nordheim conduction mechanism, is coincident with the experimental current density curve at the onset of conduction in the dielectric. Conduction proceeds when the width of that barrier is less than or equal to the tunneling distance, then electrons are able to penetrate through the barrier into the conduction band of the dielectric. As the electrons reach the position of traps within the oxynitride layer, they begin to fill them. The rate at which electrons are trapped within the oxynitride film can be described by²⁹

$$\frac{dn}{dt} = \frac{J\sigma}{q} \cdot (N_o - n), \quad (5)$$

where J is the current density within the dielectric, σ is the electron capture cross section of a trap and N_o is the total areal density of traps within the film. Also, when this expression is integrated, it gives the number of traps which are filled at a time t :

$$n(t) = N_o \left(1 - \exp \left[\frac{-J_{\text{FN}} \sigma}{q} \right] \right). \quad (6)$$

Now when electrons fill traps within the dielectric, this changes the profile of the electric field within it such that the electric field at the cathode decreases. This may be taken into account if the centroid of trapped charge, x_c , during injection is known. Assuming that electrons are preferentially trapped at nitrogen related sites in the oxynitride film, x_c can be determined from the Auger data as the position of maximum nitrogen concentration within the film. The value of x_c from Fig. 1(b) was found to be 8.5 nm. If the areal density of traps in the film at time t is $n(t)$ then the decrease in the electric field at the cathode produced by trap charging is

$$E_c = E - \left[\frac{qn(t)(d - x_c)}{\epsilon d} \right], \quad (7)$$

where d is the thickness of the dielectric and ϵ is the static dielectric constant (determined from capacitance voltage measurement).

The theoretical current density curves presented in Fig. 6 were generated from Eq. (5) iteratively using the solution (6), assuming that $N_o = 5 \times 10^{12} \text{ cm}^{-2}$ and $\sigma = 10^{-15} - 10^{-17} \text{ cm}^2$. (Similar values have also been obtained by other for oxynitride films.¹⁹) The theoretical equation for the Fowler–Nordheim current density (2) was also substituted into Eq. (6) along with the decrease in the electric field due to trap charging [Eq. (7)]. Generally, it shows a relatively close fit to the experimental curve for the oxynitride dielectric, particularly at values of electric field strength in excess of 8 MV cm^{-1} . However, it was noted that when $N_o < 5 \times 10^{12} \text{ cm}^{-2}$ the theoretical current density was greater than the experimental current density for each value of electric field in excess of 8 MV cm^{-1} and vice versa for values of $N_o > 5 \times 10^{12} \text{ cm}^{-2}$. Furthermore, when σ was chosen to be $1 \times 10^{-15} \text{ cm}^2$, the theoretical current density was found to be at least one order of magnitude less than the experimental current density and vice versa when σ was chosen to be $1 \times 10^{-17} \text{ cm}^2$.

Tao *et al.*³⁰ examined electrical conduction in silicon nitrides deposited by plasma enhanced chemical vapor deposition. In their investigation they examined three types of film: (a) Si rich Si_3N_4 , (b) a stoichiometric Si_3N_4 , and (c) an oxynitride. They suggested that the Si rich Si_3N_4 film, which consists of an abundance of Si–Si bonds, exhibits Poole–Frenkel conduction behavior. By comparison, the conduction mechanism of the stoichiometric Si_3N_4 film, which has a higher proportion of nitrogen atoms within, was said to be hopping conduction at low electric fields and Poole–Frenkel at high electric fields. Furthermore, the mechanism in the oxynitride film was said to consist of a smaller component of hopping at low electric fields, than that reported in the stoichiometric film, and a higher degree of tunneling at higher electric fields. Moreover, it was also suggested that the conduction mechanism for oxynitride films was partially Poole–Frenkel and partially Fowler–Nordheim.

Although Tao *et al.* suggested that conduction in their oxynitride dielectrics was due to both the Poole–Frenkel and Fowler–Nordheim conduction mechanisms, we do not believe that both of these mechanisms are operating within our oxynitride dielectrics. The reasons for this are twofold, first, the I - V data extracted from the oxynitride MISs were found to be polarity dependent and, second, an attempt to produce a Poole–Frenkel theoretical curve fit to the experimental data failed. The data required for the theoretical curve fit, i.e., the Poole–Frenkel proportionality constant (C_{PF}), the barrier height (ϕ_1), and the dynamic dielectric constant were extracted from the experimental Poole–Frenkel plot. Furthermore, Tao *et al.* make no attempt to produce a theoretical curve fit to their experimental data to clearly show that the Poole–Frenkel conduction mechanism is actually operating within their oxynitride dielectrics. Moreover, a theoretical model is presented in this article which suggests that

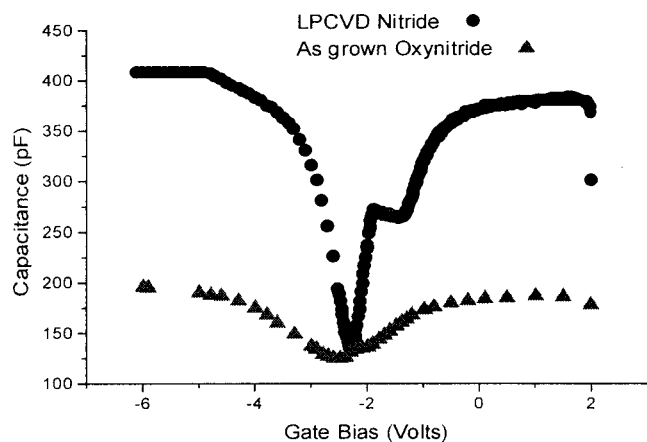


FIG. 7. Quasistatic C - V curves from typical LPCVD silicon nitride and oxidized silicon nitride (silicon oxynitride) MIS capacitors investigated in this work. The zero is suppressed to emphasize the plateau due to traps located just above and near midgap.

the conduction mechanism is due fundamentally to Fowler–Nordheim tunneling while at the same time a dynamic trapping process is also occurring. This trapping process is thought to be related to the presence of defects in the silicon nitride layer.

C. Interface electronic properties

Quasistatic C - V measurements were taken using 0.38 mm diam capacitors in order to obtain information about the electronic properties of the silicon-dielectric interface. The C - V curves for the as deposited LPCVD nitride and the as grown oxidized nitride films are shown in Fig. 7. A common feature is the presence of a ledge in the weak to strong inversion regime. As the bias applied to the gate of the MIS is swept between accumulation and inversion, the Fermi level is pinned when it passes through the region where the ledge is located. At this point, charge is filling traps and the displacement current remains constant with time. In the case of the nitride film this ledge has a trap density of $4.5 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ and stretches from 0.635 to 0.810 eV (Fig. 8),

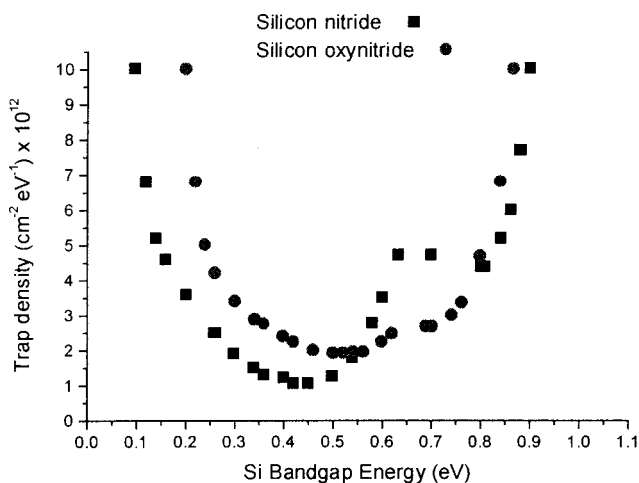


FIG. 8. Interface trap distributions calculated from the quasistatic C - V data of typical silicon nitride and silicon oxynitride MIS capacitors.

whereas in the case of the oxynitride film the ledge has a trap density of $2.3 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ and stretches from 0.619 to 0.689 eV. Therefore, oxidation of the nitride film reduces the width of the ledge and reduces the density of traps by $2 \times$.

Robertson^{31,32} in his work on silicon nitride examines the defects which are present in amorphous silicon nitride films using photoemission and electron spin resonance (ESR) measurements. He states that the main defects in amorphous silicon nitride are silicon and nitrogen dangling bonds (DBs). The silicon DB forms a sp^3 state near midgap, while the nitrogen DB forms a highly localized $p\pi$ level just above the valence band edge. From our C - V analysis of the silicon nitride and oxynitride films we know that there is a ledge of traps located just above midgap in the silicon band gap. Therefore, it is possible that these traps are actually silicon dangling bonds of the form sp^3 .

The shape of each C - V curve would suggest that there is a significant number of interface traps present in both cases. Analysis of these curves indicates that the midgap capacitance of 100–150 pF is far in excess of that which would be expected for the ideal capacitor with the same parameters, approximately 10–20 pF. By considering the equivalent circuit of a real rather than an ideal MIS capacitor, its total capacitance, C_T , can only be calculated with the inclusion of the term representing the capacitance of the interface traps, C_{it} . From the equivalent circuit, the total capacitance of a MIS capacitor is

$$C_T = \frac{C_i(C_s + C_{it})}{C_i + (C_s + C_{it})}, \quad (8)$$

where C_i is the capacitance of the dielectric and C_s is the capacitance of the silicon. Hence, if an ideal C - V curve was plotted alongside the experimental curve such that they were aligned at midgap, then the difference in height between the experimental and the ideal C - V curves is the capacitance of the interface traps, C_{it} .

The calculation of the density of states is based on a model by Kuhn.²³ The main assumption of this model is that there are few, if any, traps at the band edges. Hence, the difference between the ideal and experimental C - V curves in the accumulation region is negligible. Therefore, with the ideal curve fitted to the experimental curve in accumulation, it is possible to calculate the interface trap distribution over most of the band gap. The interface trap densities of the LPCVD nitride and the oxidized nitride films were calculated, assuming a nominal doping level of $5 \times 10^{14} \text{ cm}^{-3}$ in the p -type substrates. Also, the thickness of the deposited nitride and the oxynitride films, measured by an Applied Instruments ellipsometer, was 21 and 25 nm, respectively. The midgap interface trap density before and after oxidation was calculated to be $1.9 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$. Therefore, there is no change in the midgap interface trap density with oxidation.

IV. CONCLUSIONS

This research has focused on the development of oxynitride dielectrics by the oxidation of silicon nitride using a novel process. This type of film could be used as a gate

dielectric for thin film transistors (TFTs) on glass where high temperatures cannot be used. Other possible uses include isolating dielectrics, power metal-oxide-semiconductor field effect transistors (MOSFETs) or isolated gate bipolar transistors.

Plasma anodization of LPCVD silicon nitride gradually transforms the surface and bulk of the Si_3N_4 film into a SiO_2 film. The effect of oxidizing a uniform, nominally 20 nm thick Si_3N_4 film was to produce a three layer film "silicon oxide rich/silicon nitride rich/silicon oxide rich" of a nominal thickness of 25 nm.

As expected, the conductivity of the silicon nitride film is greater than the silicon oxynitride film, however, the trapping characteristics of the oxynitride are more temperature dependent. The activation energy required to release an electron from a trap in the oxynitride is $1.7\times$ that of the nitride film. Therefore, the trap depth in the oxynitride is twice that of the nitride and the number of electrons which are detrapped in the oxynitride at a given temperature is less than in the nitride film.

The theoretical Fowler–Nordheim J - E curve, which was modified to account for a dynamic trapping process in the oxynitride, showed a reasonably close fit to the experimental data, particularly in the high field regime above 8.5 MV/cm. However, there is some overestimation of the theoretical current density below 7 MV/cm and some underestimation above 7 MV/cm for an areal trap density, N_o , of $5\times 10^{12} \text{ cm}^{-2}$ and capture cross section, σ , of $1\times 10^{-16} \text{ cm}^2$.

Both the silicon nitride and the silicon oxynitride films have high interface trap densities of the order of $10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$. Therefore, plasma oxidation of the silicon nitride has had little effect on the interface trap density. However, the ledge which appears in the C - V curves, which is known to be due to a high density of traps located just above midgap, is reduced upon oxidation. It is thought that these traps are caused by silicon dangling bonds which form an sp^3 state near midgap.

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