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Study of Excess Silicon at Si_3N_4/Thermal SiO_2 Interface Using EELS and Ellipsometric Measurements

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The chemical composition and structure of the Si_3N_4/thermal SiO_2 interface in silicon/oxide/nitride/oxide (SONO) structures were studied by using electron energy loss spectroscopy (EELS) and ellipsometric measurements. Both experiments show the existence of excess silicon at the Si_3N_4/thermal SiO_2 interface, in the form of Si–Si bonds in the Si-rich silicon oxynitride. Wet oxidation of the as-deposited Si_3N_4 has profound effects on the interfaces in SONO structure. Mechanisms responsible for these observations are proposed based on the chemical reactions during the synthesis of the SONO structure. Particularly, we propose that the Si–Si bonds are produced by replacing nitrogen with oxygen during the oxidation of Si_3N_4. These bonds should be the responsible candidates for the positive charge accumulation in re-oxidized nitrided oxide at the hot hole injection and ionizing radiation.
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The oxide-nitride-oxide (ONO) structure has been widely used in the dynamic random access memory (DRAM) and electrical erasable programmable read only memory (EEPROM) devices. The ONO structures are used in DRAM as the dielectric in the three-dimensional stacked and trench memory capacitors instead of thermal SiO_2 and as the interpoly dielectric for multilevel metallization in complementary metal oxide semiconductors (CMOS) technology.[1,2] In floating gate EEPROM, the ONO structure is used as the dielectric between the floating gate and the control gate. This layer reduces the electronic discharge from the floating gate. The low leakage current of ONO structure (compared to SiO_2) can be attributed to electron capturing of the traps in Si_3N_4 and reduction of barrier transparency at the negatively biased electrode interface. Electron and hole localization on deep traps in the ONO structure can be used to write or erase the information in EEPROMs. Abnormally large trapping of electrons at the Si_3N_4/thermal SiO_2 interface[3-5] and hot electron and hole capturing in the ONO structure[6] are often reported experimentally. The nature of this phenomenon is still unclear. It is suggested that silicon oxynitride (SiO_xN_y) probably will be used as the gate dielectric in future memory devices for blocking boron penetration and reducing hole traps at the Si/SiO_2 interface. The traps in SiO_xN_y governed the leakage current, breakdown, and reliability. Usually SiO_xN_y is produced by thermal oxide annealing in NH_3, NO, or N_2O gas. Nitridation of SiO_2 in NH_3 results in the creation of a high density of electron traps in SiO_xN_y. To reduce the trap density, re-oxidation of SiO_xN_y usually follows after nitridation. Reoxidation results in the decrease of the electrons traps density. However, at the top interface SiO_xN_y/SiO_2 there is observed a high density of hole traps.[7] The nature of these traps is still unclear.

The aim of this paper is to investigate the physical structure of the Si_3N_4/thermal SiO_2 interface so as to understand the nature of traps at the interface and in silicon oxynitride. Two experimental techniques are employed for this purpose: electron energy loss spectroscopy (EELS) and ellipsometric measurements with chemical etching. Some preliminary results have been published.[8] This work describes a more complete and systematic investigation of excess silicon at the Si_3N_4/thermal SiO_2 interface.

Sample Preparation and Measurement

The silicon-oxide-nitride-thermal oxide (SONO) structure was fabricated on a p-type silicon with orientation <100> or <111> and resistivity of about 10 Ω cm. A thin thermal oxide of 18 or 60 Å was first grown with dry oxidation and then a low pressure chemical vapor deposition (LPCVD) Si_3N_4 was deposited on thermal oxide at 800°C using a mixture of $SiCl_4$ and NH_3. The thickness of Si_3N_4 was 150 Å for electron energy loss spectroscopy (EELS) to minimize charging effects, about 400 Å for ellipsometric measurements and 2200 Å for infrared absorption measurements. Thermal oxide on Si_3N_4 was either native or produced by wet oxidation. Native oxide formed quickly when removing the sample from the hot LPCVD reactor to the atmosphere, whereas the wet oxidation was made at 900°C for 52 min. The ellipsometric measurements were performed using step-by-step etching of SONO structures in $NH_4F:HF = 7:1$ solution at room temperature.

EELS measurements were conducted with Riber model LAS-3000 Auger electron spectrometer. The electron-beam with energy in the range of 100 to 3000 eV and 90° incident angle was used. The reflected electrons were measured at 42° with a cylinder mirror analyzer (see Fig. 1).

Electron Energy Loss Spectroscopy

In the free electron approximation, the bulk plasmon energy ($\hbar\omega_B$) is governed by the density of valence electrons (N_v) and is given by

$$(\hbar\omega_B)^2 = 4\pi\hbar^2 e^2 N_v / m^* \quad [1]$$

where e and m^* are the charge and effective mass of electron, respectively. The density of valence electrons in Si_3N_4 is governed by

$$N_v = N_A \rho \frac{n_{Si} + \frac{4}{3} n_N}{A_{Si} + \frac{4}{3} A_N} \quad [2]$$

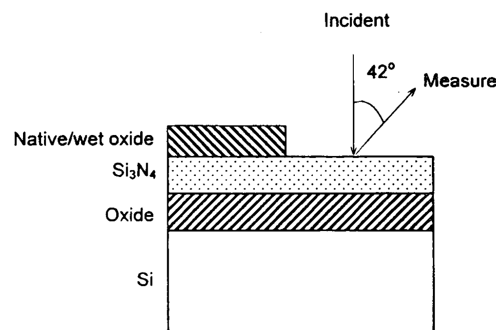

Figure 1. Illustration of sample structure and parameters for EELS measurements.

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where ρ is the Si_3N_4 atomic density, N_A is the Avogadro number, A_{si} and A_N are the atomic weights of silicon and nitrogen, respectively; n_{si} and n_N are the numbers of valence electrons per silicon and per nitrogen atom taking part in the plasmon oscillation, respectively.

Since the density of valance electrons in Si_3N_4, SiO_2, and Si are different, the bulk plasmon energies are also different in these materials. The electron mean free path (EMFP) in the solid state depends on the energy of the electrons. The higher the electron energy, the larger the EMFP. For instance at the excitation energy of 1486.6 eV, the Si 2p electrons with a binding energy of about 100 eV will have a kinetic energy of about 1380 eV and their EMFP at this kinetic energy is 21.1 Å in Si and 29.6 Å in SiO_2.[9] At excitation energy of 130 eV, the same Si 2p electrons will have a kinetic energy of about 30 eV and the mean free path is about 4 Å in Si and 7 Å in SiO_2 only.[10] Hence bulk plasmon can be studied with high energy EELS and plasmon in thin surface layer can be investigated with low excitation energy.

Figure 2 shows the XPS loss spectra of Si_3N_4, SiO_2 and Si. The bulk plasmon energies ($\hbar\omega_B$) for Si_3N_4, SiO_2, and Si are 24.0 eV (from N 1s level), 23.0 eV (from O 1s), and 17.0 eV (from Si 2p), respectively. The accuracy of this measurement is about 1 eV. A more accurate (to about 0.3 eV) value of bulk plasmon energy had also been obtained by using high-energy (3000 eV) EELS measurements, and the results are depicted in Fig. 3. As shown in Fig. 3, the values of plasmon energies are the same as those obtained by XPS measurements. In addition, multiple plasmon excitations (three plasmons in Si and two plasmons in both SiO_2 and Si_3N_4) were observed which are indicated by arrows in Fig. 3. No surface plasmon with energy of $\hbar\omega_B/\sqrt{2}$ was found. The 24.0 eV plasmon for Si_3N_4 corresponds to $n_{si} = 4$ and $n_N = 5$ at the Si_3N_4 density ρ = 3.0 g/cm³.[11]

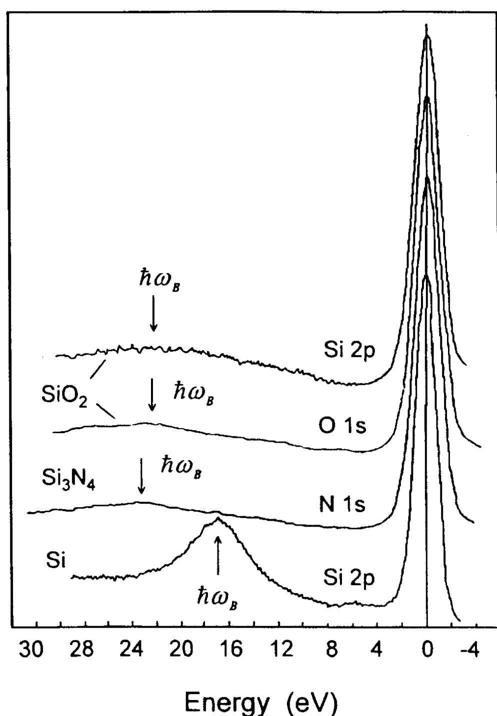

Figure 2. XPS electron energy loss spectra of SiO_2, Si_3N_4, and Si.

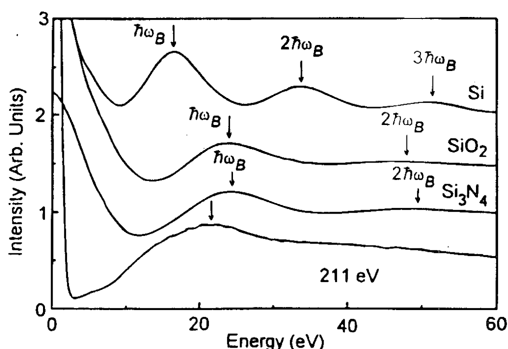

Figure 3. EELS spectra of bulk Si, SiO_2 and Si_3N_4 at electron-beam energy of 3000 eV (upper three curves) and EELS spectra with 211 eV beam energy for Si_3N_4/wet SiO_2 interface after the top oxide was etched away (bottom curve).

Value $n_N = 5$ is a result of the plasmon oscillation of (a) Si 3s, 3p, N 2p bonding; (b) N $2p_\pi$ nonbonding nitrogen electrons of top valence band; and (c) two N 2s electrons of lower valence band.[12] This result is different from the conclusions drawn by Guraya et al.[13] who reported $n_N = 3$ which corresponds to the plasmon oscillation from three p nitrogen electrons of the top valence band of Si_3N_4. To study the Si_3N_4/wet oxide interface, the top wet oxide is removed first and then a low energy (211 eV) electron-beam was used to probe the surface plasmon. As shown in Fig. 3, a wide plasmon peak with energy about 21-22 eV for Si_3N_4/wet SiO_2 interface is observed.

Similar experiments were also conducted for the Si_3N_4/native SiO_2 interface. The native oxide on Si_3N_4 was etched away by using $HF:H_2O$ = 1:30 solution. The etching rate of SiO_2 in this solution is about 1 Å/s [estimated by using X-ray photoelectron spectroscopy (XPS) measurement]. After the oxide layer was removed, EELS measurements with different electron-beam energy were conducted on the Si_3N_4 surface. The decrease of electron-beam energy for EELS measurement gives rise to a low energy shift and a widened plasmon peak. As shown in Fig. 4, a plasmon peak at an energy of about 20 eV and with a large width was found at the electron-beam energy of 100 eV at the Si_3N_4/native SiO_2 interface.

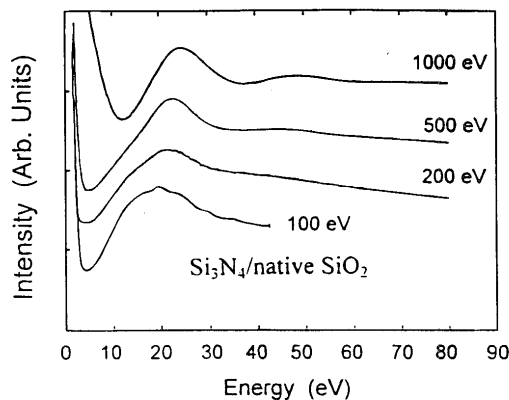

Figure 4. EELS of Si_3N_4/native SiO_2 interface at different electron-beam energies after removal of top SiO_2.

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Figure 5 shows the second derivative of EELS measurement for Si_3N_4 after the surface native and wet SiO_2 were removed. The high energy peaks with an energy of 20.3 and 21.1 eV can be seen clearly in the Si_3N_4 films which were previously covered by native and wet oxide, respectively. These peaks are attributed to the plasmon oscillation in the transition layer at the Si_3N_4/SiO_2 interface. The low energy peaks are probably due to defect excitations or interband transitions.

It is necessary to note that the second derivatives EELS are very sensitive to etching time and measurement conditions (electron beam energy and current). Plasmon losses at Si_3/N_4/native or Si_3N_4/wet SiO_2 interface with energy in the range 20-22 eV is lower than that of bulk Si_3N_4 and bulk SiO_2. Hezel and Lieske[14] found that the plasmon at Si_3N_4/native oxide interface is 19.6 eV. Lifshiz et al.[15] also reported that the plasmon at Si_3N_4 with native oxide decreases from 24 to 20 eV when the electron-beam energy changes from 2500 to 100 eV. Unfortunately, no explanation for the observation of low plasmon energy was proposed in these papers.

The decrease of the plasmon energy and the increase of the width of the peak by decreasing the electron beam energy can be explained as follows. A reduction in the electron energy results in the decrease of the EMFP and then reduces the plasmon energy relating to the plasmon losses in the transition layer at the Si_3N_4/SiO_2 interface. First-order approximation can be made by assuming the low energy plasmon peak at 100 eV in Fig. 3 is composed by two peaks corresponding to Si_3N_4 and Si. The EMFP in SiO_2 measured at energy of 70 eV is about 6.6 Å,[16] and the effective width of the "silicon" interfacial layer, roughly equal to EMFP, is in the range of 6–8 Å which is consistent with the value proposed earlier by Lifshiz et al.[15]

It was found that the nonstoichiometric silicon nitride (with excess silicon) has a plasmon energy in the range of 17 to 24 eV.[13,17] Qualitatively the decrease of plasmon energy with the increase of excess silicon concentration can be explained with the following equation

$$N_v = \rho \frac{n_{si} + x n_N}{A_{si} + x A_N} L_A \qquad [3]$$

where N_v is the density of valence electrons in SiN_x, ρ is the SiN_x atomic density, A_{Si} and A_n are atomic weights, L_A is Avogadro number, n_{Si} and n_N are the numbers of valence electrons taking part in the SiN_x plasmon oscillation. The atomic density of SiN_x decreases from 3.0 g/cm^3 (for Si_3N_4) to 2.33 g/cm^3 (for Si).

Similarly in the Si-enriched silicon oxide ($SiO_{x<2}$), the plasmon energy changes from 22 eV (stoichiometric silicon oxide) to 17 eV (silicon).[18] The decrease of plasmon energy in SiN_x and SiO_x is attributed to the increase of the Si-Si bond concentration. The decrease of plasmon energy in the transition layer at the Si_3N_4/SiO_2 interface can also be explained by the presence of Si–Si bonds at this interface.

It is more reasonable to expect that in general the transition layer at Si_3N_4/SiO_2 interface consists of silicon-enriched silicon oxynitride (Si-rich SiO_xN_y). Silicon oxynitride (SiO_xN_y) may consist only of Si–O and Si–N bonds when it is grown at excess oxygen and nitrogen environment.[19] The SiO_xN_y film without Si–Si bonds consists of five sorts of tetrahedrons, i.e., $SiO_\nu N_{4-\nu}$, $\nu = 0, 1, 2, 3, 4$. Silicon oxynitride without Si–Si bonds was found to have physical properties within the bounds of those properties in SiO_2 and Si_3N_4,[20-22] and its plasmon energy between 22.0 eV (SiO_2) and 24.0 eV (Si_3N_4). However, our experiment shows that the plasmon energy at the Si_3N_4/SiO_2 interface is in the range 20-22 eV. The discrepancy can be readily resolved by considering the excess silicon. The Si-rich SiO_xN_y consists of Si–O, Si–N, and Si–Si bonds.

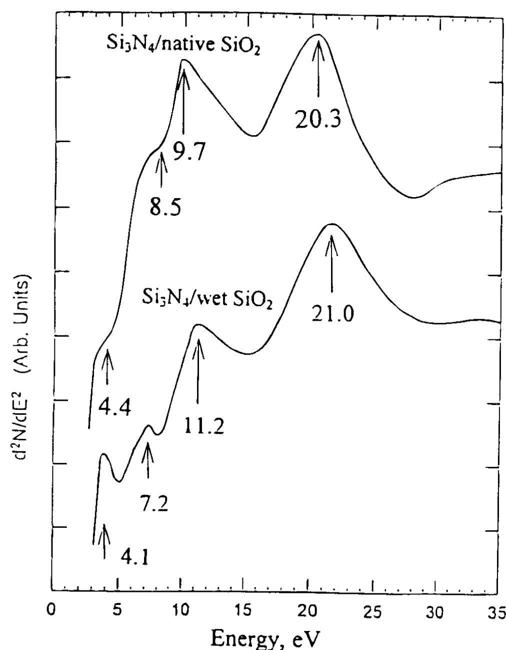

Figure 5. Second derivative of EELS of Si_3N_4/native SiO_2 and Si_3N_4/wet SiO_2 interfaces measured at an electron-beam energy of 200 eV after the top oxide layer was removed.

Ellipsometric Measurements

Multiple angle ellipsometric measurements were carried out using a laser beam with a wavelength of 632.8 nm. Our parameter extraction software for the ellipsometer can restore four parameters simultaneously.[23] The measurement process is as follows. Top-down layer-by-layer etching and measurements were first performed until the Si substrate was reached. Then bottom-up parameter calculation process began, i.e., the lowest layer parameters, n_1, d_1, (oxide on silicon) was calculated first and in the following steps four parameters (n_1, d_1 and n_2, d_2) were calculated simultaneously. During the measurements, we assumed that the layers being measured are transparent and homogenous and the interlayer interface is abrupt. The etching time for each step was kept as small as possible to have a better resolution.

Before wet oxidation, the two-layer model was used in the calculation and the properties of the lower layer found in previous step was not considered. After wet oxidation, parameters n_i (where $i = 3, 4, 5$) of the upper layers were determined with the single-layer model where the results found at previous steps were also taken into account. With wet oxidation, significant changes of the optical parameters (refractive index and thickness) are found in all regions (oxide on silicon, silicon nitride, and oxide on nitride regions) when compared to the previous ones.

The parameters n and d of thermal oxide on silicon were independently verified many times for structures with native oxide and with wet oxidation. Unfortunately, accuracy of the refractive index is poor if the film thickness is less than 100 Å. The accuracy is within ±2% from median value of n_1 and ±5% from median value of d_1. The variations give rise from (*i*) measurement errors, (*ii*) precision of ellipsometer, and mainly (*iii*) exactness of the same positioning at each step.

It is well known that Si, SiO_2, and Si_3N_4 have distinct values of refractive indexes; their typical values are 3.42, 1.46, and 1.96, respectively. Enriching SiN_x or SiO_x with excess silicon results in the increase of their refractive indexes.[22] Figure 6 shows the refractive index as a function of the depth of the ONO structure before (with native oxide) and after wet oxidization. The refractive index $n = 2.1$ of the interfacial layer of Si_3N_4/wet oxide system is significantly larger than 1.96 which is typical for the bulk of amorphous Si_3N_4. Although we did not detect any refractive index larger than

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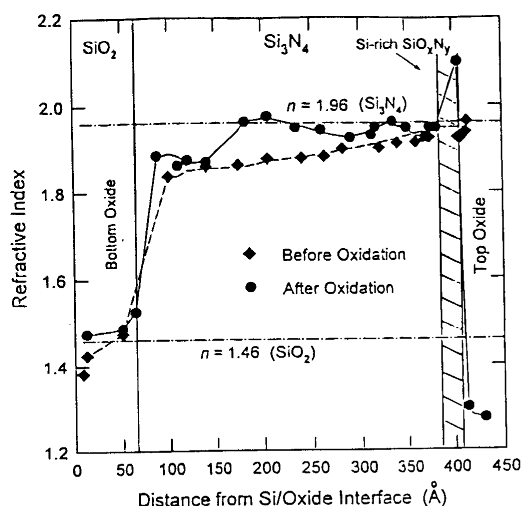


Figure 6. Refractive index of $Si/SiO_2/Si_3N_4/SiO_2$ with native oxide (before oxidation) and wet oxide after oxidation) at different depths.

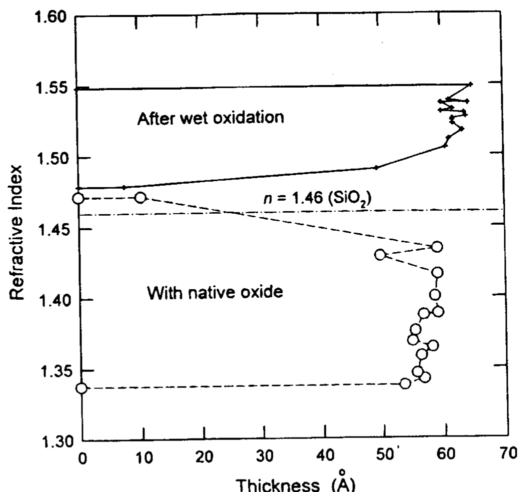


Figure 7. Comparison of restored thickness and refractive index of the bottom thermal oxide in $Si/SiO_2/Si_3N_4/SiO_2$ structure before (with native oxide) and after wet oxidation.

1.96 before wet oxidization, we cannot ascertain that there is no excess silicon at the interface as the step resolution for etching and ellipsometric measurements is still quite large.

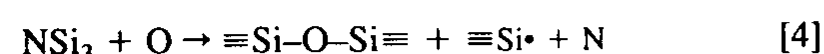
To sum up, we have found from both EELS and ellipsometric measurements that excess silicon (Si–Si bonds) exist at the Si_3N_4/thermal SiO_2 interface. The interfacial layer may be in the form of SiN_x, SiO_x, or Si-rich SiO_xN_y. Wet oxidation of Si_3N_4 results in the change of optical properties in Si_3N_4, bottom SiO_2, and top SiO_2 films (see Fig. 6 and 7). In addition, oxidation also results in the change of etching rate of Si_3N_4, bottom oxide, and top oxide (see Fig. 8). In the following section possible mechanisms for these changes are discussed in detail.

Change of Dielectric Refractive Index during ONO Structure Synthesis

In this section, possible chemical reactions are discussed and the change of optical properties of dielectric layers in ONO structures at different fabrication steps are explained.

Creation of Si–Si bonds at Si_3N_4/thermal SiO_2 interface.—The excess Si–Si bonds were observed in the present work at both Si_3N_4/native SiO_2 and Si_3N_4/wet SiO_2 interfaces. In following sections the possible reactions for both structures are discussed.

Native oxidation.—Generally the Si–Si bond creation during the Si_3N_4 oxidation in dry atmosphere can be understood based on the Mott rule. According to this rule, each Si atom in SiO_2, Si_2N_4, or SiO_xN_y is coordinated by four O and/or N atoms, each O atom in SiO_2, SiO_xN_y is coordinated by two Si atoms and each N atom in Si_3N_4 or SiO_xN_y is coordinated by three Si atoms.[22] Substitution of N atom by O atom during Si_3N_4 dry oxidation accompanies the creation of a three-coordinated silicon atom with an unpaired electron $\equiv Si\bullet$

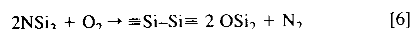


$$NSi_3 + O \rightarrow \equiv Si{-}O{-}Si\equiv + \equiv Si\bullet + N \quad [4]$$

Two such silicon atoms with unpaired electrons result in the creation of an Si–Si bond, namely

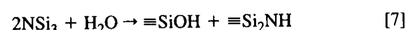
$$\equiv Si\bullet + \bullet Si\equiv \rightarrow \equiv Si{-}Si\equiv \quad [5]$$

The overall reaction can be written as



$$2NSi_3 + O_2 \rightarrow \equiv Si{-}Si\equiv 2\ OSi_2 + N_2 \quad [6]$$

Wet oxidation.—The chemical reactions relating to the Si–Si bond creation during wet oxidation are more complicated. Possible reactions are given below[24-26]



$$2NSi_3 + H_2O \rightarrow \equiv SiOH + \equiv Si_2NH \quad [7]$$

$$\equiv Si_2NH + H_2O \rightarrow \equiv SiOH + \equiv SiNH_2 \quad [8]$$

$$\equiv SiNH_2 + H_2O \rightarrow \equiv SiOH + NH_3 \quad [9]$$

$$\equiv Si{-}O{-}Si\equiv + NH_3 \rightarrow \equiv Si_2NH + H_2 \quad [10]$$

$$\equiv SiOH + \equiv SiOH \rightarrow \equiv Si{-}Si\equiv + H_2 + O_2 \quad [11]$$

$$\equiv Si{-}O{-}Si\equiv + H_2 \rightarrow \equiv SiOH + \equiv SiH \quad [12]$$

$$\equiv SiOH + \equiv SiH \rightarrow \equiv Si{-}Si\equiv + H_2O \quad [13]$$

Reactions 6-13 describe, on the atomic scale, the creation of Si–Si bonds at the Si_3N_4/SiO_2 interface during the silicon nitride oxidation in terms of chemical bond rearrangements. The Si–Si bonds at Si_3N_4/SiO_2 interface are part of the $SiSi_\alpha O_\beta N_\delta$ tetrahedrons in

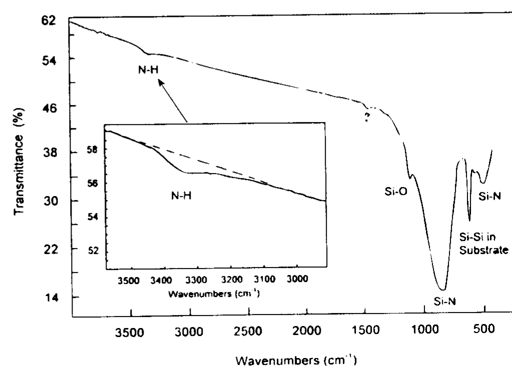


Figure 8. Infrared absorption of Si/SiO_2 (60 Å)/Si_3N_4 (2200 Å)/SiO_2 structure before (solid) and after (dashed) wet oxidation.

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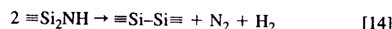
which α, β, δ = 0, 1, 2, 3, 4, and $\alpha + \beta + \delta = 4$. These tetrahedrons build the Si-rich SiO_xN_y.

Increase of Si_3N_4 refractive index after oxidation.—As shown in Fig. 6, the refractive index of bulk Si_3N_4 increases after wet oxidation. This effect can be explained with the out-diffusion of hydrogen from Si_3N_4 during the wet oxidation and the creation of Si–Si bonds. For Si_3N_4 with a high concentration of NH bonds, the release of hydrogen and nitrogen from the nitride was observed experimentally after the sample was annealed in vacuum.[27] This result could be due to the following reaction



$$2 \equiv Si_2NH \rightarrow \equiv Si\text{–}Si\equiv + N_2 + H_2 \quad [14]$$

According to Eq. 14, hydrogen is released from silicon nitride. This process will accompany the creation of the Si–Si bond. The Si–Si bond creation during the annealing of Si_3N_4 has been confirmed experimentally with the shift of the fundamental absorption edge to the lower energy side in infrared measurements.[22,27] As measured with the infrared absorption spectroscopy the silicon nitride (after synthesis with native oxide) has an absorption band in infrared region and centered at 3330 cm^{-1} which is attributed to the absorption of Si_2NH bond (see Fig. 8). The concentration of NH bonds in this sample is about 2×10^{21} cm^{-3}. Wet oxidation results in the decrease of NH bonds and reduces the infrared absorption. The proposed explanation also agrees with the decrease of etching rate of silicon nitride after oxidation. It is well known that the decrease of hydrogen bond density in silicon nitride would also result in the decrease of the etching rate.[20]

Optical properties of bottom oxide.—Figure 7 indicates the refractive index of the bottom SiO_2 on Si before and after wet oxidation. The data depicted in Fig. 7 clearly shows the changes of SiO_2 properties after wet oxidation. Both the thickness and the refractive index of the bottom SiO_2 increase after the Si_3N_4 film was oxidized. The average refractive index before wet oxidation is less than 1.46 (a typical value for thermal oxide on silicon). It is greater than 1.46 after wet oxidation, however.

The refractive index of dry thermal oxide with a thickness of about 50 Å before Si_3N_4 deposition was 1.46. Deposition of Si_3N_4 results in the decrease of oxide refractive index (Fig. 7) and the increase of etching rate (Fig. 8). These two phenomena can be explained by the oxide hydrogenation (reaction 12). The hydrogen atoms, which escape from Si_3N_4 bottom layers (reaction 14) during Si_3N_4 deposition further react with SiO_2 and produce Si–OH and Si–H bonds. Hydrogen-containing oxide often has a smaller refractive index. It is well known than low temperature (CVD) SiO_x:H film which contains a large density of hydrogen (and appeared as SiOH and SiH bonds) has refractive indexes smaller than the thermal SiO_2.[28] Similarly, the refractive index of PECVD SiN_x:H film with a large density of N–H and Si–H bonds has a refractive index smaller than that of a nitride with a small density of hydrogen.[29] In addition, it is well known that the increase of hydrogen contamination in SiO_x:H and SiN_x:H film results in the decrease of etching rate. These results agree with the experimental results depicted in Fig. 9.

Optical properties of bottom oxide after Si_3N_4 oxidation.—The increase of bottom oxide refractive index after Si_3N_4 deposition can be explained with the following mechanisms.

Nitridation of bottom oxide at Si_3N_4 oxidation.—Nitrogen escaped from the bulk Si_3N_4 during wet oxidation can diffuse into the bottom oxide and results in the following reaction

$$3 \equiv Si_2O + 2N \rightarrow 2 \equiv Si_3N + 3\,O \quad [15]$$

The replacement of O atoms in the bottom SiO_2 by N atoms results in the formation of oxynitride. It is well known that the refractive index will be increased by increasing the nitrogen concentration in SiO_xN_y.[20] The oxygen, which is released after the replacement reaction 15, diffuses into SiO_2 and results in the further oxidation of silicon substrate. This effect explains the increase of the bottom SiO_2 thickness after the silicon nitride was oxidized.

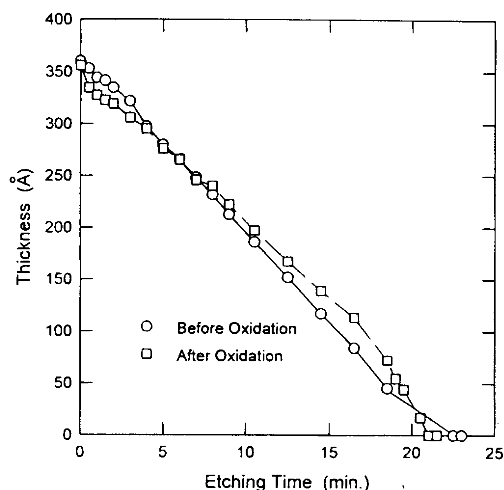


Figure 9. Plot of the thickness of $Si/SiO_2/Si_3N_4/SiO_2$ structure vs. the etching time for the structure before and after wet oxidation.

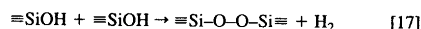
Reduction of bottom oxide after Si_3N_4 oxidation.—Another possible mechanism for the increase of the bottom oxide refractive index after Si_3N_4 oxidation is the enriching of SiO_2 by excess silicon due to creation of oxygen vacancies as proposed Devine,[30] the reaction is

$$\equiv Si\text{–}O\text{–}Si\equiv \rightarrow \equiv Si\text{–}Si\equiv + O \quad [16]$$

Oxygen diffusion from the bottom SiO_2 into Si results in the creation of $SiO_{x<2}$ and oxidation of silicon substrate.

It is possible that both mechanisms 15 and 16 take part in the increase of the refractive index and further growth of the bottom oxide. However, present results cannot differentiate between reactions 15 and 16.

Optical properties of oxide produced by Si_3N_4 oxidation.—The refractive index of the top oxide in the ONO structure is smaller than that of the dry thermal oxide on silicon (see Fig. 6). The low value of the refractive index in the top oxide may be due to the hydrogenation effect of the top oxide, i.e., creation of Si–OH and Si–H bonds according to reaction 12. Excess oxygen contamination in the top oxide may also give rise to the low value of the refractive index. Excess oxygen may exist in the form of the peroxide bridge Si–O–O–Si. The peroxide bridge forms on the top oxide at high temperatures according to the following reaction[31]



$$\equiv SiOH + \equiv SiOH \rightarrow \equiv Si\text{–}O\text{–}O\text{–}Si\equiv + H_2 \quad [17]$$

Discussion

The direct evidence of the existence of excess silicon at Si_3N_4/native SiO_2 interface in ONO structures was obtained by qualitative analyses using XPS measurement with high-resolution chemical etching.

The evidence of excess silicon at the Si_3N_4/wet and Si_3N_4/native SiO_2 interfaces in this work are the low values of plasmon energy and large width of plasmon peak at the interface. Our newly proposed model can also interpret the low value plasmon energy obtained by others.[14,15] The plasmon with energy 19.6 eV at Si_3N_4/native oxide interface, obtained by Lieske and Hezel,[14] can be attributed to the existence of Si-rich SiO_xN_y at the interface. For Si_3N_4 with the native oxide, the plasmon energy decreases from 24 to 20 eV by lowering the electron-beam energy from 2500 to 100 eV. This was observed previously by Lifshiz et al.[15] and can be explained by the existence of Si-rich SiO_xN_y at the Si_3N_4/native SiO_2

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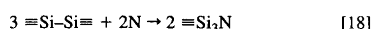
interface. However, Lieske and Hezel[32] obtained a low "bulk plasmon" energy (18.6 eV) in Si_3N_4. This result is inconsistent with our data and the value (24.0 eV) obtained by Lifshiz et al. The discrepancy can be explained as follow. In Lieske and Hezel's experiments,[32] the "bulk plasmon" energy was determined by bombarding the Si_3N_4 and with Ar^+ ions. It was shown that the Ar^+ bombardment of Si_3N_4 would reduce the nitrogen concentration on the surface, forming Si-rich Si_3N_4.[33] The decrease of $SiN_{x<2}$ density results in the decrease of plasmon energy.[13,17]

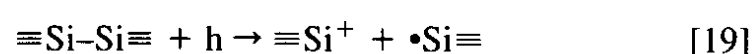
On the other hand, the ellipsometric measurements of SONO structures do not provide direct evidence of the existent of excess silicon at Si_3N_4/native SiO_2 interface. Similar results were observed by others.[34,35] However, excess silicon does exist at the Si_3N_4/wet SiO_2 interface. With spectroscopic ellipsometric measurements, Theeten et al.[36] found that there exists an amorphous silicon layer of about 12 Å between the nitride/native oxide layers in the SONO structures. Silicon accumulates after the sample was annealed in NH_3 at 900°C. This observation was explained with the interaction between excess Si–Si bonds and nitrogen according to the following reaction



$$3 \equiv\text{Si–Si}\equiv + 2\text{N} \rightarrow 2 \equiv\text{Si}_3\text{N} \qquad [18]$$

Reaction 18 also explains the removal of Si–Si bonds after the SiO_2 was nitrided.[38] Reaction 18 also explains the accumulation of excess silicon at the Si_3N_4/native SiO_2 interface in SONO structures. Although excess silicon was not observed by using ellipsometric measurements,[34,35] AES profile interface had shown the existence of a notable amount of excess silicon at Si_3N_4/wet SiO_2 interface.[36] Hence, a more systematic ellipsometric investigation of excess silicon in SONO structures is needed in order to clarify this discrepancy.

It is well known that there are some $\equiv Si_3N$ species on the top surface of SiO_xN_y after nitridation of SiO_2,[38] and it was shown that, at the top surface of reoxidized SiO_xN_y, the existence of the a high density of E' centers was observed.[7] E' centers are created after a hole was captured on a Si–Si bond according to reaction



$$\equiv\text{Si–Si}\equiv + \text{h} \rightarrow \equiv\text{Si}^+ + \bullet\text{Si}\equiv \qquad [19]$$

It is natural to propose that the Si–Si bonds at the SiO_xN_y/thermal SiO_2 interface are created by replacing nitrogen atoms with oxygen atoms according to reaction 6. The numerical simulation of Si–Si electronic structure shows that these defects in silicon oxide and silicon nitride may act as electron and hole traps.[39-42] These results together can be used to explain the abnormally large electron and hole capturing at the Si_3N_4/thermal SiO_2 interface.[3-6] However, the results obtained in the present work show that the oxidation mechanism of Si_3N_4 is more complicated than that based only on transformation of Si–N bonds in Si_3N_4 into Si–O bonds. In fact, some unusual kinetics of Si_3N_4 oxidation are observed.[43,44] Hence we suggest that the creation of Si–Si bond at Si_3N_4 oxidation should be taken into account.

Conclusions

Excess silicon at Si_3N_4/thermal native and wet oxide interfaces has been qualitatively studied by using EELS and ellipsometric measurements. The main results are as follows.

1. With EELS measurements we found that the plasmon energy of the transition layer at the Si_3N_4/thermal oxide interface is lower than that of Si_3N_4 and SiO_2. Plasmon peaks at the interface have larger widths than those of Si_3N_4 and SiO_2.

2. Ellipsometric measurements show a large value (2.1) of the refractive index in the transition layer. It is the evidence of the existence of excess Si–Si bonds at Si_3N_4/wet SiO_2 interface.

3. Wet oxidation of Si_3N_4 results in the increase of the refractive index of the bottom oxide and nitride in ONO structures. Changes of refractive index of the dielectric layers in ONO structure after the wet oxidation of Si_3N_4 are qualitatively explained in terms of chemical reaction in solid state.

4. The above observations are interpreted in terms of the Si-rich SiO_xN_y layer at the Si_3N_4/thermal SiO interface. The estimated width of this layer is in the range of 6-8 Å.

5. The Si–Si bond creation during Si_3N_4 oxidation is explained with the Mott rule. Replacement of the threefold coordinated N atom by twofold coordinated O atom result in the creation of Si–Si defects.

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