

# Excess silicon at the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface

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(Received 7 July 1997; accepted for publication 25 November 1997)

Using electron energy loss spectroscopy, X-ray photoelectronic spectroscopy, and ellipsometry measurements, a large number of Si-Si bonds at the Si<sub>3</sub>N<sub>4</sub>/thermal SiO<sub>2</sub> interface is confirmed. After etching away the surface SiO<sub>2</sub> of reoxidized Si<sub>3</sub>N<sub>4</sub>, we found at the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface that the plasmon energy on the surface is 20 eV which is smaller than the bulk plasmon of either Si<sub>3</sub>N<sub>4</sub> (24.0 eV) or SiO<sub>2</sub> (23.0 eV). From ellipsometric measurement, a large value of the refractive index ( $n = 2.1$ ) in the Si<sub>3</sub>N<sub>4</sub>/wet SiO<sub>2</sub> interface layer was obtained. The effective width of the Si-rich interfacial layer is estimated to be in the range of 6–8 Å. We propose that the excess silicon at the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface is created by replacing nitrogen atoms with the oxygen atoms during the oxidation of Si<sub>3</sub>N<sub>4</sub>. Based on these observations and on numerical simulation, a hypothesis is proposed to explain the abnormally large electron capturing at the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface observed previously and the accumulation of positive charge at the top interface of the nitrated oxide under ionizing irradiation. © 1998 American Institute of Physics. [S0003-6951(98)02704-1]

The Si/SiO<sub>2</sub> interface structure has been studied extensively in the past decades as it has a great influence on the operation of microelectronic devices. One of the major results is that Si-Si bonds in the thermal oxide near the Si/SiO<sub>2</sub> interface were found.<sup>1</sup> These Si-Si bonds are responsible for the hole capturing in metal-oxide-semiconductor (MOS) structures during ionizing irradiation.<sup>2</sup> On the other hand, the amorphous silicon nitride/amorphous thermal oxide (Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub>) interface is also important in silicon devices. The double layer insulator (Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub>) has been widely used in silicon-oxide-nitride-silicon (SONOS) and metal-oxide-nitride-silicon (MONOS) structures because the amorphous Si<sub>3</sub>N<sub>4</sub> is able to localize electrons and holes. Abnormally large trapping of electrons at the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface in SONOS and MONOS structures was observed.<sup>3,4</sup> However, the nature of this phenomenon is still unclear so far. The aim of this work is to study the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface and to identify the origin of the anomalous large electron capturing at this interface.

The starting material is a *p*-type ⟨111⟩ orientation silicon with resistivity of about 10 Ω cm. A thin thermal oxide of 60 Å was first grown with dry oxidation and then a low-pressure chemical vapor deposition (LPCVD) Si<sub>3</sub>N<sub>4</sub> was deposited on the thermal oxide using silicon tetrachloride and ammonia mixture at 800 °C. The ratio of SiCl<sub>4</sub>/NH<sub>3</sub> was 0.1. The thickness of the Si<sub>3</sub>N<sub>4</sub> film was 150 Å for the electron energy loss spectroscopy (EELS) and X-ray photoelectronic spectroscopy (XPS) measurements to minimize charging effects. For the ellipsometric measurement, the nitride layer was about 350 Å. The thermal oxide on the Si<sub>3</sub>N<sub>4</sub> was produced by either a “native” process or wet oxidation. The native oxide of the Si<sub>3</sub>N<sub>4</sub> was formed by exposing the silicon wafer to evaporated nitride from a hot reactor to room atmosphere.

The thickness of the native oxide on the Si<sub>3</sub>N<sub>4</sub> film was about 10 Å.<sup>5</sup> Wet oxidation of the Si<sub>3</sub>N<sub>4</sub> film was made at 900 °C for 50 min in water steam. To study the upper Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface, the top thermal oxide was etched in 10% HF:H<sub>2</sub>O solution.

The Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface was studied by XPS, EELS and ellipsometry. Excitation of XPS was made by Al *K*<sub>α</sub> monochromatized radiation with energy of 1486.6 eV. For ellipsometric measurements, step by step etching in NH<sub>4</sub>F:HF=7:1 solution was conducted and multiple angle incident measurements were carried out using a laser beam with  $\lambda = 6328$  Å.

From XPS loss spectra the bulk plasmon energies of the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub>/Si structure were obtained. The spectrum was taken for Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub>/Si, SiO<sub>2</sub>/Si and Si. The bulk plasmon energies ( $\hbar\omega_B$ ) for Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub> and Si are 24.0 eV (from N 1*s* level), 23.0 eV (from O 1*s*) and 170 eV (from Si 2*p*), respectively. The accuracy of this measurement is about 1 eV. In this work, a more accurate (about 0.3 eV) value of the bulk plasmon energy was obtained by using high energy (3000 eV) EELS and is depicted in Fig. 1. As shown in Fig. 1, the values of plasmon energies the same as the XPS measurements for Si, SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> were obtained. In addition, multiple plasmon excitation (five plasmons in Si and two plasmons in SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>) was observed which is indicated by the arrows in Fig. 1. No surface plasmon with energy  $\hbar\omega_B/\sqrt{2}$  was observed.

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

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

where  $m^*$  is the electron effective mass. The density of the valence electrons in Si<sub>3</sub>N<sub>4</sub> is governed by

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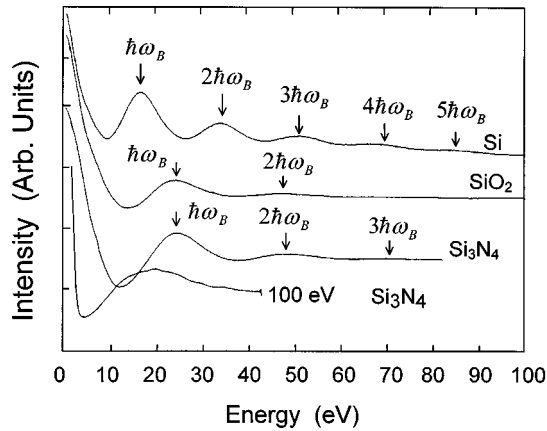


FIG. 1. High energy (3000 eV) EELS spectra of Si, SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> (upper three traces) and low energy EELS (100 eV) of Si<sub>3</sub>N<sub>4</sub> after the removal of surface native oxide.

$$N_V = N_A \rho \frac{n_{Si} + \frac{4}{3}n_N}{A_{Si} + \frac{4}{3}A_N}, \quad (2)$$

where  $\rho$  is the Si<sub>3</sub>N<sub>4</sub> 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.

According to Eq. (2), the 24.0 eV plasmon for Si<sub>3</sub>N<sub>4</sub> corresponds to  $n_{Si}=4$  and  $n_N=5$  at density  $\rho=3.0 \text{ g/cm}^3$ .<sup>6</sup> Value  $n_N=5$  is a result of the plasma oscillation of (a) Si 3s, 3p, N 2p bonding, (b) N 2p<sub>π</sub> nonbonding nitrogen electrons of the top valence band, and (c) two N 2s electrons of the lower valence band. This result is different from the conclusions drawn by Guraya *et al.*<sup>7</sup> who reported  $n_N=3$  which corresponds to the plasmon oscillation from four s, p silicon electrons and three p nitrogen electrons of the top valence band of Si<sub>3</sub>N<sub>4</sub>.

After the native thermal oxide was removed, an EELS measurement with different electron beam energies was conducted on the Si<sub>3</sub>N<sub>4</sub>/ surface. A decrease of electron beam energy for EELS results in a lower energy shift and widening of the plasmon peak. As shown in Fig. 2, a plasmon peak at an energy of about 20 eV with a large width was found at an electron beam energy of 100 eV. The energy location of this

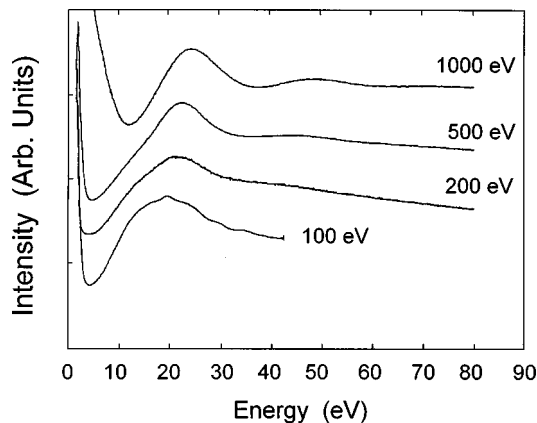


FIG. 2. EELS spectra of Si<sub>3</sub>N<sub>4</sub> surface at different electron beam energies after removal of the native oxide layer.

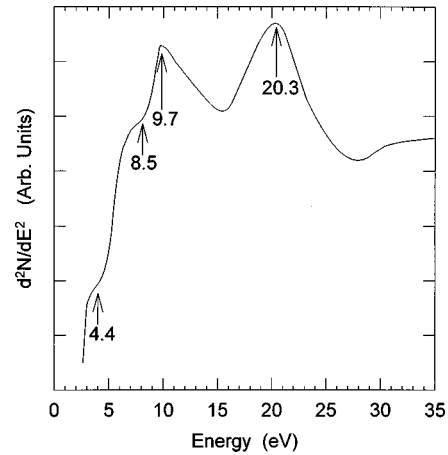


FIG. 3. Second derivative of EELS spectra of Si<sub>3</sub>N<sub>4</sub> measured at 200 eV.

peak is smaller than that of the first bulk plasmon in Si<sub>3</sub>N<sub>4</sub> or SiO<sub>2</sub>. A decrease of plasmon energy of Si<sub>3</sub>N<sub>4</sub> by lowering the electron beam energy was observed previously by Lifshiz, Kotlar and Saranin.<sup>8</sup> However, no explanation was proposed. Figure 3 shows the second derivative of EELS at 200 eV for measurement on Si<sub>3</sub>N<sub>4</sub> after the surface native oxide was removed. The high energy peak with energy of 20.3 eV can be seen clearly. This peak is attributed to the plasmon oscillation at the upper Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface. The low energy peaks are due to the defect excitation or interband transitions.

Figure 4 depicts the refractive index profile of the Si<sub>3</sub>N<sub>4</sub>/oxide structure with native surface oxide or after wet oxidation. These data were obtained by step-by-step etching and ellipsometric measurements. For the sample before wet oxidation, the refractive index ( $n$ ) of the nitride is in the range of 1.95–1.96. After wet oxidation, the refractive index increases. Particularly at the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface, the refractive index increases significantly to about 2.1. The large  $n$  value at the re-oxidized interface, according to Bolotin *et al.*<sup>6</sup> is attributed to the silicon nitride enriched by excess silicon, i.e., SiN<sub>*x*</sub> ( $x \approx 1.2$ ). This composition corresponds to about 10 atomic percent of excess silicon atoms in the silicon nitride, namely the interface layer consists of Si-N and Si-Si bonds. As shown in Fig. 4, no Si-Si bonds at the Si<sub>3</sub>N<sub>4</sub>/native

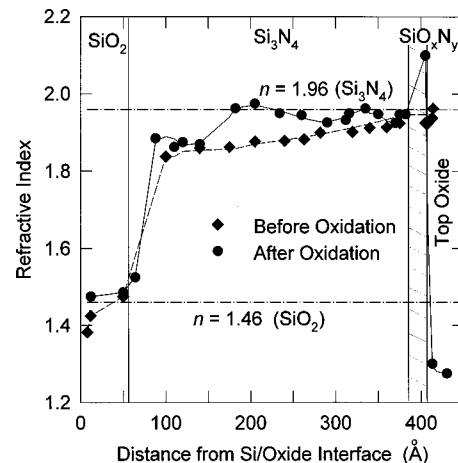
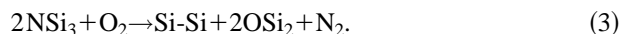


FIG. 4. Profile of the refractive index of the Si/SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> structure. The distance was measured from the Si/SiO<sub>2</sub> interface.

oxide interface can be observed. This result may be due to the large step size used in the profiling. However, a Si-Si bond at the Si<sub>3</sub>N<sub>4</sub>/native oxide interface was observed previously by XPS using a smaller step size for etching<sup>9</sup> and suggests that the structure of the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface should be silicon oxynitride enriched by excess silicon. The oxynitride consists of five sorts of tetraedra SiSi<sub>α</sub>O<sub>β</sub>N<sub>δ</sub> where α, β, δ=0, 1, 2, 3, 4 and α+β+δ=4. In conventional silicon oxynitride SiO<sub>x</sub>N<sub>y</sub>, only Si-N and Si-O bonds were found.<sup>10,11</sup> However, in the thin transitional oxynitride layer between Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> (both wet and native oxide), in addition to Si-N and Si-O bonds, Si-Si bonds are also found in this work. We propose that the excess silicon (Si-Si bonds) at the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface should be due to the replacement of nitrogen atoms with oxygen atoms during the oxidation according to the following reaction:



This reaction is governed by the Mott rule<sup>10-12</sup> which suggests that each nitrogen atom in Si<sub>3</sub>N<sub>4</sub> should be coordinated by three silicon atoms. Substitution of nitrogen by oxygen results in the formation of OSi<sub>2</sub> groups in the oxide side and is accompanied by the creation of a silicon dangling bond, i.e., ≡Si• at the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface. Two such silicon atoms with unpaired electrons result in the creation of a Si-Si bond.

The plasmon energy lowering in SiN<sub>x</sub>, according to Eq. (1), was attributed to the decrease of valence electron concentration.<sup>7,13</sup> However, we are inclined to believe that the decrease in valence electron concentration is due to the increase of Si-Si bonds which is found in the thin interfacial layer (several angstroms) between Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub>. For EELS measurements with higher electron beam energy, the contribution of the interfacial layer to the excited layer is small and the plasmon energy is determined by the bulk properties of Si<sub>3</sub>N<sub>4</sub>. By decreasing the beam energy of EELS, the contribution of this interfacial layer increases and the effective plasmon energy decreases. A first order approximation can be made by assuming the plasmon peak at 100 eV is composed of two peaks with the same amplitude corresponding to Si<sub>3</sub>N<sub>4</sub> and Si. With this approach, the mean free path of the electron in SiO<sub>2</sub> measured at an energy of 70 eV is about 6.6 Å.<sup>14</sup> Since only a trace amount of excess silicon is found and the effective "silicon" interfacial layer should be very thin, the width of this interfacial layer can be estimated roughly to be in the range of 6–8 Å. This estimation is consistent with the value proposed by Lifshiz, Kotlar and Saranin.<sup>8</sup>

A polaron model of multiphonon electron and hole trapping on the neutral Si-Si bond in Si<sub>3</sub>N<sub>4</sub> was proposed.<sup>11,12,15-17</sup> Recent numerical simulation also shows that the Si-Si bonds in Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> do not only capture holes

(as Si-Si bonds in SiO<sub>2</sub>) but also electrons.<sup>18,19</sup> Suzuki *et al.*<sup>3</sup> and Aganin *et al.*<sup>4</sup> also confirmed that the Si-Si bonds at the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interfaces are responsible for the large amount of electron capturing in MONOS and SONOS structures. Hence, the memory properties of SONOS and MONOS structures are governed by Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface traps rather than by the bulk properties of Si<sub>3</sub>N<sub>4</sub>.

In conclusion, XPS, EELS, and ellipsometric measurements on the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface layer were made. EELS of Si<sub>3</sub>N<sub>4</sub>/native oxide and ellipsometry results of Si<sub>3</sub>N<sub>4</sub>/wet oxide interfaces indicate the existence of Si-Si bonds at the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interfaces. We propose that the excess silicon in this structure is due to the replacement of nitrogen atoms with oxygen atoms during the oxidation. We further estimate that the effective width of this interface layer is in the range of 6–8 Å. The existence of Si-Si bonds at the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface explains the abnormally large electron capturing at the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface and the hole capturing at the top interface of the nitrated oxide. These results support the conjecture proposed earlier that Si-Si bonds in Si<sub>3</sub>N<sub>4</sub> are trap centers for both electrons and holes.<sup>15-18</sup>

The authors would like to thank B. I. Fomin and L. I. Mahnanova for their help in sample preparation.

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