PACS numbers: 61.43.-j, 61.66.Fn, 68.35.Dv, 71.55.Jv

## Structure of silicon/oxide and nitride/oxide interfaces

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DOI: 10.0007/011000179.2009090.092	DOI: 10.336	/UFNe.0179.200909a	.0921
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<u>Abstract.</u> We systematize and generalize modern concepts on the atomic structure of silicon/insulator (Si/SiO<sub>2</sub>, Si/SiO<sub>x</sub>N<sub>y</sub>) and insulator/insulator (Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub>) interfaces in the structures underlying the operation of silicon devices.

### 1. Introduction

The unique physical properties of the crystalline Si/amorphous SiO<sub>2</sub> interface provide the foundation for the development of planar silicon microelectronic technology. The active element of a silicon microcircuit is a metal–insulator–semiconductor (MIS) transistor, a device operating based on the modulation of silicon conductivity as a function of the electric field. Si/SiO<sub>2</sub> is currently the most studied solid–solid interface type.

The three key insulators used in silicon-based devices are silicon dioxide (SiO<sub>2</sub>), silicon oxynitride (SiO<sub>x</sub>N<sub>y</sub>), and silicon nitride (Si<sub>3</sub>N<sub>4</sub>) [1, 2]. The dioxide has a low density of surface states on the Si/SiO<sub>2</sub> interface and a low (10<sup>17</sup> cm<sup>-3</sup>) concentration of defects (traps) in the bulk. Electron and hole capture in the dioxide layer causes charge accumulation and leads to the device degradation. Silicon nitride, by contrast, has a high (10<sup>19</sup>-10<sup>20</sup> cm<sup>-3</sup>) concentration of electron and hole traps. Silicon oxynitride (SiO<sub>x</sub>N<sub>y</sub>) combines the advantages of silicon dioxide with those of silicon nitride.

The amazing fact about  $SiO_2$  is that along with microelectronics, some forms of life are heavily dependent on it. In fact, in many forms of animal and vegetable life, pure  $SiO_2$ forms the cell membrane and the outer solid shell (exoskeleton). Silicon and oxygen are the two most abundant elements

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Received 21 October 2008, revised 17 April 2009 Uspekhi Fizicheskikh Nauk **179** (9) 921–930 (2009) DOI: 10.3367/UFNr.0179.200909a.0921 Translated by E G Strel'chenko; edited by A M Semikhatov

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in the Earth's crust, their  $SiO_2$  combination accounting for about 95% of the crust mass. Monocell organisms form their cell membranes via molecule-by-molecule self-assembly of  $SiO_2$  from an ambient-temperature water solution. These organisms, known as diatoms, exist in thousands of symmetrical morphological patterns [3]. The electron microscopy image of a SiO<sub>2</sub> exoskeleton shown in Fig. 1 reveals details about 100 nm across [4]. It is amazing that, with 400 million years of history behind organisms this small, the modern electronics industry has nothing of the kind in its arsenal, and it will take some time from now before it has biologically selfassembled materials, including SiO<sub>2</sub> structures.

Silicon nitride is used as an insulator in the three-layer oxide–nitride–oxide (ONO) system. Each ONO layer is typically  $\approx 50$  Å thick. The effective dielectric constant of the structure is higher than the dielectric constant of the oxide (for SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>,  $\varepsilon = 3.85$  and 6.50 respectively). The ONO structure has wide application as an insulator in the multilayer lead arrangement in silicon integrated circuits. It has a lower leak current, a higher breakdown voltage, and a higher reliability compared to the oxide; the reason is that the electric field in the insulator decreases near the injection



Figure 1. Scanning electron spectroscopy image of a SiO<sub>2</sub> skeleton.

An important application of ONO structures is as a memory medium in the energy-autonomous metal–oxide– nitride–oxide–semiconductor (MONOS) flash memory cell, a device capable of storing information for ten years at 85 °C [5, 6]. A MONOS memory cell is an MIS field effect transistor using an ONO structure as a subgate insulator. Under a positive or negative bias applied to the gate, electrons or holes are injected from the silicon substrate into the nitride layer and are caught by traps, leading to a shift in the threshold voltage as they accumulate. The electron and hole lifetimes of more than 10 years in deep traps ( $\approx 1.5$  eV) in silicon nitride allow building flash memory by using the localization effect in the nitride. Currently, a terabit (10<sup>12</sup> bit per crystal) nitride flash memory cell is being developed.

A recent trend in the field effect transistor design is that subgate silicon nitride is replaced with insulators with a high dielectric constant (so-called *alternative* insulators), such as HfO<sub>2</sub>, HfAlO, HfSiO<sub>x</sub>, HfO<sub>x</sub>N<sub>y</sub>, ZrO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, and Al<sub>2</sub>O<sub>3</sub> [7, 8]. Because of the high density of surface states at the interface between silicon and an alternative insulator, the technology used is first to grow a SiO<sub>2</sub> or SiO<sub>x</sub>N<sub>y</sub> layer  $\approx 5$  Å thick on the silicon surface and then to coat it with an approximately 5 Å thick layer of an alternative insulator. In recent years, the application of synchrotron radiation, among other factors, including the use of theoretical quantum mechanical calculations, has enabled considerable progress in understanding the structure of Si/SiO<sub>2</sub>,  $Si/SiO_rN_v$ , and  $Si_3N_4/SiO_2$  interfaces. The purpose of this paper is to review the current understanding of the three most important interfaces used in silicon electronics.

### 2. Si/SiO<sub>2</sub> interface

The density of broken  $\equiv$  Si<sub>3</sub>Si  $\bullet$  bonds on a free Si surface is  $\approx 8 \times 10^{14}$  cm<sup>-2</sup>. Here and in what follows, we use - to denote a normal two-electron bond and • to denote an unpaired electron. The surface state density at the Si/thermal oxide interface is  $\sim 10^{12}$  cm<sup>-2</sup>. It is now established that surface states at the Si/SiO2 interface are 3-fold Si coordinated paramagnetic Si atoms with an unpaired electron  $(\equiv Si_3Si_{\bullet}, broken silicon bonds)$ , the so-called P<sub>b</sub> centers with the gyromagnetic factor g = 2.006 [9, 10]. Annealing in hydrogen results in the interface surface state density decreasing to 10<sup>10</sup> cm<sup>-2</sup> due to saturation of broken bonds by hydrogen via the reaction  $\equiv$  Si<sub>3</sub>Si • + H  $\rightarrow$   $\equiv$  Si<sub>3</sub>SiH. The interaction with hydrogen, while decreasing the surface state density, is at the same time a source of instability. At high temperatures,  $\equiv$  Si<sub>3</sub>SiH bonds break up in the reaction  $\equiv$  Si<sub>3</sub>SiH  $\rightarrow \equiv$  Si<sub>3</sub>Si • + H, leading to the formation of surface  $\equiv$  Si<sub>3</sub>Si • states. It is a well-established empirical fact that because of the replacement of hydrogen by deuterium D during the annealing process, more stable  $\equiv$  Si<sub>3</sub>SiD bonds form.

The optical properties of thermal oxide on silicon have been investigated by the ellipsometry method in numerous studies. The refractive index of thick oxide ( $\approx 100$  nm) is 1.46, and that of silicon is 3.44 ( $\lambda = 6328$  Å). As thermal oxide on silicon decreases in thickness, its refractive index increases [12]. Specifically, decreasing the thickness from 8 nm to 2 nm increases the refractive index from 1.52 to 2.00 — an effect similar to that observed in Ref. [13]. Figure 2a presents multiple-angle ellipsometry results on the refractive



index variation through a 32 Å thick layer of  $SiO_2$  on silicon [14]. The index increases from 1.45 at the outer surface of the oxide to 1.61 at the distance 3 nm from the  $Si/SiO_2$  interface.

The increase in the refractive index with decreasing the  $SiO_2$  thickness is explained in [13] based on the Grunthaner model [15]. It is known that different allotropic modifications of  $SiO_2$  differ in density and in the number of closed  $SiO_2$  rings [16]. The refractive index of  $SiO_2$  is higher when fewer Si-O-Si bonds exist in the ring. According to the Grunthaner–Gonon model, the outer surface of the oxide contains a large number of rings (6 to 7); closer to the  $Si/SiO_2$  boundary, the rings decrease in number, leading to an increased refractive index (Fig. 2b) [15].

Plasmon spectroscopy used to study the Si/SiO<sub>2</sub> interface has shown [17] that the plasmon energy varies from 17.0 eV (for Si) to 22.0 eV (for SiO<sub>2</sub>) depending on the composition [18, 19]. Electron energy loss spectra due to the plasmon excitation are shown in Fig. 3 for the SiO<sub>2</sub> thickness range 0-50 Å [17]. It is seen that the thinner the oxide, the higher the plasmon energy, which can be attributed to a higher oxygen content x in SiO<sub>x</sub>, i.e., to the fact that the oxide is enriched in excess silicon as it decreases in thickness.

In Ref. [20], the authors used infrared (IR) vibrational spectroscopy to probe the structure of thermal oxide on





**Figure 3.** Plasma loss in Si/SiO<sub>2</sub> with the oxide thickness 50 Å. The parameter is the distance from the Si/SiO<sub>2</sub> interface. The notation -5 Å' refers to the distance 5 Å from the interface toward the silicon. Positive values are measured toward the oxide.

silicon whose thickness was in the range 6 to 30 Å. Figure 4 shows the IR absorption spectra of films of different thicknesses for normally and obliquely incident radiation. For normal incidence, only transverse optical (TO) phonons are seen in the spectrum, whereas in the oblique case, longitudinal optical (LO) phonons are also observed. Both types show a decrease in frequency (red shift) as the oxide thickness decreases from 30 to 6 Å.

It is known that the IR absorption peak moves down in frequency when  $SiO_x$  is enriched with silicon [21]. Figure 5 shows the vibrational spectra of  $SiO_x$  of varying compositions x. Different compositions (stoichiometries) are obtained by oxidizing the initial  $SiO_x$  in oxygen at different temperatures. Oxidization causes x to increase. Decreasing x (enriching  $SiO_x$  with excess silicon) shifts the IR absorption peak toward lower frequencies. With this knowledge, the red shift in IR absorption with decreasing the oxide thickness on silicon can be interpreted (see Ref. [20]) using the idea that the thin layer of thermal oxide is enriched with excess silicon, i.e., is in fact  $SiO_x$ . The underlying assumption here is that decreasing the thickness from 30 to 6 Å has the effect of enriching the oxide with excess silicon.

Photoelectron spectroscopy using synchrotron radiation provided unique data on the structure of the Si/SiO2 interface [15, 21, 22]. The photoelectron spectra of the O 1s and Si 2p levels of the oxide are shown in Fig. 6 [15] for the thicknesses 49 and 23 Å. The splitting of the O 1s and Si 2p levels is interpreted as being due to the presence in the oxide of closed Si-O bonds with different dihedral angles. Numerical calculations show that decreasing  $\theta$  from 180° to 90° leads to an increase from 0.4 to 0.6q in the charge transfer to Si-Obonds (see Fig. 7, which is reproduced from Ref. [15]). The dependence of the Si–O–Si angle on the charge transfer  $\Delta q$ was calibrated in terms of the chemical shifts of the Si 2p and O 1s levels. This establishes a correspondence between the energies of the Si 2p and O 1s levels, on the one hand, and the dihedral angle  $\theta$  on the other hand, thus providing information on the structure of the transition layer at the Si/SiO<sub>2</sub> boundary. Based on the experimentally observed intensity ratio, the transition in question is from predominantly sixmember rings (characteristically found in  $\alpha$  quartz in oxide 49 Å thick) to four-member ( $\theta = 125^{\circ}$ ) keatite rings. Low binding energies result in weak signals, which correspond to SiSiO<sub>3</sub> and SiSi<sub>2</sub>O<sub>2</sub> tetrahedra (see Fig. 6).

Figure 8 shows synchrotron radiation photoelectron spectra of the Si/SiO<sub>2</sub> structure with 6 Å thick SiO<sub>2</sub> on a (100) silicon substrate, measured at the excitation energy 130 eV for the excitation radiation incident at angles 0° or 60° [22]. 6 Å is exactly the thickness at which the oxide will potentially be used in combination with alternative insulators [8]. The zero energy is taken at the position of the atomic Si 2p peak in the silicon substrate (SiSi<sub>4</sub> tetrahedron). The peak seen at the energy  $\approx$  26.5 eV corresponds to the silicon substrate (tetrahedron SiSi<sub>4</sub>) and is split due to the spin–doublet coupling. The 23 eV Si<sup>4+</sup> peak corresponds to stoichiometric SiO<sub>2</sub>, tetrahedron SiO<sub>4</sub>. Three in-between energy peaks Si<sup>3+</sup>, Si<sup>2+</sup>, and Si<sup>1+</sup> are attributable to the presence of SiO<sub>x</sub>



Figure 4. IR absorption spectra of a thermal oxide film 6.3–31.0 Å thick on silicon for the normal (a) and oblique (b) beam incidence.



**Figure 5.** IR transmission spectra of SiO<sub>x</sub> films fabricated (1) and oxygenannealed (2) at 450 °C for 1 hr; (3) at 600 °C for 1 hr; (4) at 700 °C for 0.5 hr; and (5) at 900 °C for 0.5 hr.



Figure 6. Photoelectron spectra of Si 2p and O 1s levels in 49 or 23 Å thick oxide on silicon.

suboxides at the Si/SiO<sub>2</sub> boundary: the tetrahedral SiO<sub>3</sub>Si, Si<sub>2</sub>O<sub>2</sub>Si, and Si<sub>3</sub>OSi, respectively. These direct experiments unambiguously indicate the presence of excess silicon in the oxide close to the silicon boundary. This means that the oxide film is enriched with silicon, which, as we discuss below, can serve as a hole trapper. The possible consequences of traps in the oxide include the capture of holes (i.e., the accumulation of positive charge), as well as a threshold voltage shift in and degradation of the field transistor.

Optical absorption studies using synchrotron radiation [23] have provided independent evidence for excess silicon in



**Figure 7.** Charge transfer to the Si–Si bond as a function of the dihedral angle Si–O–Si. Shown at the top is the chemical shift of the Si 2p level. The dashed line is the average dihedral angle in  $\alpha$ -SiO<sub>2</sub>.



Figure 8. Photoelectron spectra of the Si 2p level in Si/SiO<sub>2</sub> with the oxide thickness 6 Å for 130 eV excitation radiation incident at  $0^{\circ}$  (a) and  $60^{\circ}$  (b).

the form of  $O_3 \equiv Si - Si \equiv O_3$  bonds (oxygen vacancies) or  $O_3 \equiv Si - Si - Si \equiv O_3$  defects (oxygen divacancies) in a thermal oxide layer (14-45 Å thick) on silicon. It is known that in SiO<sub>2</sub>, an  $O_3 \equiv Si - Si \equiv O_3$  bond and a divacancy have the respective absorption lines at 7.6 eV and 6.5 eV [24-28]. The last reference gives conclusive experimental results on the subject. The optical absorption spectra of thin oxide on silicon derived from reflection spectra [23] are shown in



Figure 9. Optical absorption spectra of thermal oxide 14-45 Å thick on silicon. Dashed line: melt quartz; dotted line: exponential tail.

Fig. 9. The absorption features at 6.5 eV and 7.6 eV are respectively due to the Si–Si–Si and Si–Si defects, the corresponding defect concentrations being  $4 \times 10^{14}$  cm<sup>-2</sup> and  $8 \times 10^{14}$  cm<sup>-2</sup>.

## 3. Si/SiO<sub>x</sub>N<sub>y</sub> interface

There is currently a trend to replace dioxide SiO<sub>2</sub> with silicon oxynitride  $SiO_x N_y$  in MIS devices; the advantages of the latter are that it has a higher dielectric constant, blocks the diffusion of boron from the polysilicon gate, and is more reliable due to enhanced stability against the formation of surface states and positive charge in the insulator. Oxinitride is fabricated either by oxidizing silicon in NO, N<sub>2</sub>O or annealing thermal SiO<sub>2</sub> in NO, N<sub>2</sub>O, NH<sub>3</sub> [14]. The structure of silicon oxinitride  $SiO_x N_y$  fabricated by nitrogenizing thermal SiO<sub>2</sub> in ammonia NH<sub>3</sub> at 1000 °C was studied in [29] (Fig. 10). The chemical shift observed and the shape of the Si 2p level qualitatively point to random bonding as a model of the oxinitride structure [16], which means that the compound consists of five (binomially distributed) tetrahedron types: SiO<sub>4</sub>, SiO<sub>3</sub>N, SiO<sub>2</sub>N<sub>2</sub>, SiON<sub>3</sub>, and SiN<sub>4</sub>. The structure of silicon oxinitride is described by the Mott law, according to which each silicon atom is coordinated by four nitrogen and/or oxygen atoms, each oxygen atom is coordinated by two silicon atoms, and each nitrogen atom is coordinated by three silicon atoms.

Oxinitride obtained by oxidizing silicon in  $N_2O$  [30] presents a different situation. The photoelectron spectroscopy of Si 2p levels in this oxinitride shows that the chemical composition of the compound is closer to that of SiO<sub>2</sub>



Figure 10. X-ray photoelectron spectra of the Si 2p level in Si/SiO<sub>2</sub>, Si/Si<sub>3</sub>N<sub>4</sub>, and Si/SiO<sub>x</sub>N<sub>y</sub> structures obtained by ammonia nitrogenization.



Figure 11. X-ray photoelectron spectra of the Si 2p level in  $Si/SiO_xN_y$  structures obtained by the oxidation of Si in nitrious oxide N<sub>2</sub>O.

(Fig. 11) [30]. In Fig. 11, the Si 2p peak at 98.5 eV corresponds to the silicon substrate, and the peak position of 102.5 eV is the same as in  $SiO_2$ . At the same time, the SiO<sub>0.82</sub>N<sub>0.90</sub> and Si<sub>3</sub>N<sub>4</sub> peaks are shifted towards lower energies. The insulator obtained by the oxidization of Si in  $N_2O$  is not pure SiO<sub>2</sub>: the photoelectron spectra of the N 1s levels shown in Fig. 12 [30] exhibit a weak signal that shows the presence of nitrogen in the compound. Of much interest is how high the barrier for holes is at the silicon/oxinitride interface. The photoelectron valence band spectra of the  $Si/SiO_v N_v$  structures fabricated by the oxidization of Si in N<sub>2</sub>O are shown in Fig. 13 for two oxinitride thicknesses, 16 and 24 Å [30]. The oxinitride spectra are obtained by subtracting those of the silicon substrate. It is seen that the photoelectron spectra of oxinitride look much like those of the  $SiO_2$  valence band. The energy barrier at the silicon/ oxinitride interface is  $4.35 \pm 0.20$  eV, the same as found previously for the hole barrier at the Si/SiO<sub>2</sub> interface [31-33]. By measuring the Fowler-Nordheim injection from silicon into silicon oxinitride, the electron barrier was estimated [30] to be 2.9 eV (see Fig. 14). This is consistent with what a similar method yields for Si/SiO<sub>2</sub> [34], but less than 3.15 eV, a barrier obtained with internal photoemission



Figure 12. X-ray photoelectron spectra of the N 1s level in the  $Si/SiO_x N_y$  structure obtained by the oxidation of Si in N<sub>2</sub>O.



Figure 13. X-ray photoelectron spectra of the valence band of the  $Si/SiO_xN_y$  structure obtained by the oxidation of Si in N<sub>2</sub>O.

[35]; the discrepancy is due to the electron spectrum quantization in silicon at the  $Si/SiO_2$  interface [34].

It is known that positive charge is accumulated in the  $Si/SiO_2$  structure due to the capture of holes by Si-Si defects in  $SiO_2$  via the reaction [36]

$$\equiv \mathrm{Si} - \mathrm{Si} \equiv + \mathrm{h} \to q \equiv \mathrm{Si} \bullet^{+} \mathrm{Si} \equiv .$$
 (1)



Figure 14. Room temperature I–V characteristics of  $Si/SiO_xN_y/Al$ .

The process of hole capture by a neutral diamagnetic Si–Si defect leads to the formation of a positively charged paramagnetic E' center  $\equiv$  Si • +Si  $\equiv$  [37]. The higher stability of silicon oxinitride with respect to charge accumulation was explained in terms of the Mott rule [38]. The interaction of nitrogen with Si–Si defects during the growth of oxinitride leads to the breaking of Si–Si bonds and the formation of electrically neutral Si–N bonds via the reaction

$$3 \equiv \mathrm{Si} - \mathrm{Si} \equiv + 6 \,\mathrm{N} \rightarrow 6 \equiv \mathrm{Si} - \mathrm{N} = . \tag{2}$$

By comparing the synchrotron radiation photoelectron Si 2p spectra of the  $Si/SiO_2$  interface measured after oxidization and after annealing in N<sub>2</sub>O, it was found in [39] that the concentration of Si–Si bonds decreases after annealing. This favors the picture that according to reaction (2), Si–Si bonds change into Si–N ones due to the interaction with nitrogen.

The decrease in the density of  $\equiv$  Si • surface states on the Si/SiO<sub>x</sub>N<sub>y</sub> interface is also related to the formation of Si–N bonds via the reaction (Fig. 15) [30]

 $\equiv \mathrm{Si} - \mathrm{Si} \equiv + \equiv \mathrm{Si} + 3\mathrm{N} \rightarrow 3 \equiv \mathrm{Si} - \mathrm{N} = .$ (3)

## 4. Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface

Silicon nitride  $Si_3N_4$  is second to  $SiO_2$  as a key insulator for silicon devices. The double- and triple-layer oxide/nitride and oxide/nitride–oxide structures are currently used as insulators in main storage memory capacitors and are also regarded as an alternative to  $SiO_2$  as a subgate insulator, generating much interest in the structure of the  $Si_3N_4/SiO_2$  interface. Silicon oxide on  $Si_3N_4$  either is fabricated on purpose by thermal oxidation or, alternatively, grows as 'natural oxide.' An important finding is the formation of excess superstoichiometric silicon on the  $SiO_2/Si_3N_4$  boundary; this fact is well proved by ellipsometry experiments and is also seen from characteristic electron energy loss (CEEL) spectra.

An ellipsometry study of the Si/SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> structure was performed in Refs [40, 41], where a lower oxide 60 Å in thickness was fabricated by thermally oxidizing silicon, and a 400 Å thick Si<sub>3</sub>N<sub>4</sub> layer was deposited by the pyrolysis of the SiCl<sub>4</sub>–NH<sub>3</sub> mixture. The top oxide on the nitride was prepared by thermal oxidation in wet oxygen at 900 °C (*wet* 



Figure 15. Interaction with a nitrogen atom removes a  $P_b$  center located at the Si/SiO<sub>2</sub> interface.

*oxide*) or grew on the surface of the nitride at room temperature (*natural oxide*). The wavelength used was 632.8 nm. Using the layer-by-layer etching technique, the refractive indices of individual layers were measured, giving values in the range 1.85 to 2.00 for silicon nitride (Fig. 16) [40, 41] and 2.1 for the silicon nitride/top thermal oxide interface, the latter value being characteristic of silicon-enriched silicon nitride SiN<sub>x</sub> [16].

A CEEL experiment involves sending a monochromatic beam of electrons onto a sample. The vast majority of the electrons are elastically reflected from the sample, giving rise to what is known as the 'elastic peak.' The reflected spectrum also exhibits peaks due to inelastically reflected electrons, their energy being lost in interband (valence-to-conduction)



Figure 16. Refractive index distribution in the  $Si/SiO_2/Si_3N_4/SiO_2$  ONO structure.

transitions and to the excitation of plasma oscillations (plasmons). The energy  $\hbar\omega_b$  of a bulk plasmon is given by

$$(\hbar\omega_{\rm b})^2 = 4\pi\hbar^2 e^2 \, \frac{N_{\rm v}}{m^*} \,, \tag{4}$$

where  $m^*$  is the effective electron mass. The density of valence electrons  $N_v$  is given by

$$N_{\rm v} = N_{\rm A}\rho \, \frac{n_{\rm Si} + (4/3)n_{\rm N}}{A_{\rm Si} + (4/3)A_{\rm N}} \,, \tag{5}$$

where  $\rho$  is the density of Si<sub>3</sub>N<sub>4</sub>,  $N_A$  is the Avogadro constant,  $A_{\rm Si}(A_{\rm N})$  is the atomic weight of silicon (nitrogen), and  $n_{\rm Si}(n_{\rm N})$ is the number of silicon (nitrogen) valence electrons involved in plasma oscillations. Because SiN<sub>4</sub>, SiO<sub>2</sub>, and Si have different densities of valence electrons  $N_{\rm V}$ , they have different plasmon energies. The electron escape depth in a solid depends on the electron energy. For example, in SiO<sub>2</sub>, electrons with energies  $\sim 3000 \text{ eV}$  and  $\sim 100 \text{ eV}$  have the respective escape depths  $\approx 35$  Å and  $\approx 5$  Å. Therefore, decreasing the electron energy decreases the thickness of the layer being analyzed, thus providing a means to obtain information on the plasmon energy and hence on the depth variation of the layer chemical composition. A schematic of a plasma spectroscopy experiment on the SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> interface is shown in the inset of Fig. 17 [40]. In this experiment, the oxide on the Si<sub>3</sub>N<sub>4</sub> surface was etched, the electron beam was directed normal to the surface, and the scattered electrons were analyzed at the angle 42°. Figure 17 presents the results of the experiment, i.e., the energy dependence of the scattered electron intensity for Si, SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub> and the SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> interface. The respective plasmon energies in Si, SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> are 17.0 eV, 22.0 eV, and 24.0 eV, all measured to within  $\pm 0.3$  eV for the electron energy 3000 eV under conditions allowing the study of the bulk properties of a solid. Also shown in Fig. 17 are the results of measuring the plasmon energy at the  $SiO_2/Si_3N_4$  interface at the beam energy 211 eV; the plasmon energy is found to be 21 eV. Figure 18 presents plasma spectroscopy results on the SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> interface for different electron beam energies. A decrease in the electron energy from 1000 eV to 100 eV causes a decrease in the



Figure 17. Plasma loss in Si,  $SiO_2$  and  $Si_3N$ . Inset: schematic of a plasma spectroscopy experiment on the  $Si_3N_4/SiO_2$  interface.



Figure 18. Plasmons at the  $Si_3N_4/SiO_2$  interface for different incident electron beam energies.

plasmon energy. Figure 19, reproduced from Ref. [18], shows the second derivative of the CEEL spectrum for the  $Si_3N_4$ /wet oxide interface. The respectively plasmon energies at the  $Si_3N_4$ /wet oxide and  $Si_3N_4$ /natural oxide interfaces are 21.0 eV and 20.3 eV.

Photoelectron spectroscopy results of plasma loss in a silicon-enriched nitride  $SiN_x$  are presented in Fig. 20. In nonstoichiometric Si-enriched nitride  $(SiN_{x<4/3})$ , the plasmon energy decreases from 24 eV in Si<sub>3</sub>N<sub>4</sub> to 17 eV in Si. The density of valence electrons and the concentration of silicon in  $SiN_x$  are related by

$$N_{\rm v} = \rho \, \frac{n_{\rm Si} + x n_{\rm N}}{A_{\rm Si} + x A_{\rm N}} \, N_{\rm A} \,, \tag{6}$$

where  $\rho$  and SiN<sub>x</sub> are the density and the composition parameter of SiN<sub>x</sub>. The atomic density of SiN<sub>x</sub> decreases



Figure 19. Second derivative of the electron energy loss spectrum at the  $Si_3N_4/SoO_2$  interface.



Figure 20. Plasma loss in  $SiN_x$  as measured by photoelectron spectroscopy.

from  $\rho = 3.0 \text{ g cm}^{-3}$  in Si<sub>3</sub>N<sub>4</sub> to 2.33 cm<sup>-3</sup> in Si [42]. Equations (4)–(6) help explain why the plasmon energy in SiN<sub>x</sub> decreases as the content of excess silicon increases. In SiO<sub>x</sub>, as in SiN<sub>x</sub>, the plasmon energy decreases with increasing the silicon content [19]. The plasmon energy decreases as SiN<sub>x</sub> and SiO<sub>x</sub> are enriched with excess silicon due to the increased concentration of Si–Si bonds. Hence, the formation of excess, nonstoichiometric silicon reduces the plasmon energy at the SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> interface. As is shown by Auger spectroscopy [18], silicon-enriched silicon oxinitride forms at the SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> interface.

The formation of excess silicon (Si–Si bonds) at the  $SiO_2/Si_3N_4$  interface is understood, in accordance with the Mott rule, as the substitution of oxygen for nitrogen atoms during the oxidization of  $Si_3N_4$  [38]. As a result, because a nitrogen atom in  $Si_3N_4$  is coordinated by three silicon atoms and an oxygen atom in  $SiO_2$  by two, Si–Si bonds form via the reaction

$$\begin{split} & 2 \equiv Si_3N + 2O \rightarrow 2 \equiv Si_2O + 2 \equiv Si \bullet + 2N, \\ & \equiv Si \bullet + \bullet Si \equiv \to \equiv Si - Si \equiv . \end{split}$$

The formation of Si–Si bonds at the SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> interface is confirmed in electron paramagnetic resonance (EPR) experiments [43], in which an EPR signal due to a positively charged Si–Si bond—the so-called E' center—was observed at the interface. It is experimentally established that an excess negative charge (electrons) and an excess positive charge (holes) accumulated at the SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> interface [43]. The positive charge accumulation proceeds via reaction (1), implying that Si–Si bonds (or generally excess silicon) act as traps for electrons and holes in silicon nitride and ONO structures.

### 5. Conclusions

This review summarizes the current understanding of the structure of the silicon/insulator (Si/SiO<sub>2</sub>, Si/SiO<sub>x</sub>N<sub>y</sub>) and insulator/insulator (Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub>) interfaces, which underlie the operation of MIS devices. In recent years, high-resolution photoelectron spectroscopy (in particular, its synchrotron radiation implementation), as well as electron spectroscopy and quantum chemical calculations, have greatly contributed to the structural knowledge of these interfaces.

 $Si/SiO_2$  is presently the most studied solid-solid interface. Synchrotron radiation photoelectron spectroscopy has provided definitive evidence of the existence of excess superstoichiometric silicon in the oxide close to the interface. This excess silicon (in the form of Si–Si bonds) produces traps for holes, the traps that determine the reliability of silicon devices.

The experimental observation that the refractive index of thermal oxide on silicon increases upon decreasing its thickness is attributed to the fact that the number of Si–Si bonds in a closed ring varies along the thickness of SiO<sub>2</sub>. Whether excess silicon can or cannot explain the decrease in the refractive index of the oxide upon increasing the oxide thickness remains an open question.

The fact that thermal oxide is nitrogenized due to the interaction of nitrogen with excess silicon leads to the removal of silicon–silicon bonds. This effect is used to decrease the concentration of hole traps in the insulator.

It is established that charge is predominantly localized in an ONO structure at the  $Si_3N_4/SiO_2$  interface. Traps at the  $Si_3N_4/SiO_2$  interface are responsible for the memory effect in metal/oxide/nitride/oxide/semiconductor structures that are used in developing terabit flash memory silicon chips. The available data suggest that the excess superstoichiometric silicon in the form of Si—Si bonds accounts for the localization of electrons and holes in MONOS structures.

Acknowledgements. This work was supported by the RFBR grant No. 16621a and the integration project No. 70 SB RAS.

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