Atomic structure of the amorphous nonstoichiometric silicon oxides and nitrides

V A Gritsenko

DOI: 10.1070/PU2008v051n07ABEH006592

Contents

1. Introduction	699
2. Atomic structure of amorphous SiO ₂	699
3. Atomic structure of amorphous Si ₃ N ₄	702
4. Atomic structure of silicon oxynitride $SiO_x N_y$	702
5. Atomic structure of nonstoichiometric silicon oxide SiO _x	705
6. Atomic structure of Si-rich silicon nitride SiN _x	706
7. Conclusions	708
References	708

<u>Abstract.</u> In addition to amorphous SiO₂ and Si₃N₄, the two key dielectric film materials used in modern silicon devices, the fabrication technology of nonstoichiometric SiO_xN_y, SiN_x, and SiO_x compounds is currently under development. Varying the chemical composition of these compounds allows a wide range of control over their physical — specifically, optical and electrical — properties. The development of technology for synthesizing such films requires a detailed understanding of their atomic structure. Current views on the atomic structure of nonstoichiometric silicon nitrides and oxides are reviewed and summarized.

1. Introduction

The amorphous forms of silica (SiO_2) and silicon nitride (Si_3N_4) are the two key dielectric materials currently used in silicon devices [1]. When deposited on Si, thermal SiO₂ (i.e. SiO₂ obtained by oxidizing silicon) provides a low density ($\approx 10^{10}$ cm⁻²) of surface states at the Si/SiO₂ interface. Due to high barriers at the Si/SiO₂ interface, leak currents in the oxide are low, whereas strong electron scattering results in a high breakdown field strength (2×10^7 V cm⁻¹). The concentration of defects in SiO₂ is at a low level of $10^{15} - 10^{17}$ cm⁻³. The presence of defects in SiO₂ causes the localization of silicon microcircuits.

Silicon nitride, on the contrary, possesses a high number density ($\sim 10^{19} - 10^{20}$ cm⁻³) of electron and hole traps. The

V A Gritsenko Institute of Semiconductor Physics, Siberian Branch of the Russian Academy of Sciences

Prosp. ak. Lavrent'eva 13, 630090 Novosibirsk, Russian Federation Tel. (7-383) 333 38 64. Fax (7-383) 333 27 71 E-mail: grits@isp.nsc.ru

Received 17 March 2008 Uspekhi Fizicheskikh Nauk **178** (7) 727 – 737 (2008) DOI: 10.3367/UFNr.0178.200807c.0727 Translated by E G Strel'chenko; edited by A Radzig energies of the traps fall in the range of $\approx 1.5-2.0$ eV, and the electrons and holes trapped are kept localized at 400 K for more than 10 years — a phenomenon known as the memory effect [2]. The silicon nitride memory effect is widely used in developing silicon-based reprogrammable memory devices that are capable of preserving information even when switched off (so-called flash memory) [3] and which can presumably replace the magnetic, optical, and hard discs of present-day computers. Although the memory effect in Si₃N₄ has over a three-decade history of study and use [2–4], the nature — or more specifically the atomic and electronic structure — of the traps it relies on remains unclear.

The band gap of SiO₂ is $E_g = 8.0$ eV [1]. Enriching the oxide with silicon leads to the formation of SiO_x , silicon suboxides whose band gap decreases with decreasing oxygen content, reaching $E_g = 1.6$ eV in amorphous silicon (a-Si). Enriching silicon nitride with excess silicon decreases the band gap from $E_g = 4.5 \text{ eV}$ in Si₃N₄ to $E_g = 1.6 \text{ eV}$ in a-Si. In silicon oxynitride $SiO_x N_y$, which consists of Si-O and Si-N bonds, the band gap ranges from 4.5 eV to 8.0 eV. Thus, the physical (optical and electrical) properties of silicon oxides and nitrides can be varied widely by varying the chemical composition of the compounds. Despite this, however, the atomic structure of the nonstoichiometric oxides and nitrides of silicon is as yet not fully understood. The goal of this review is to summarize what is known about the atomic and electronic structure of the amorphous silicon oxides and nitrides of varying composition.

2. Atomic structure of amorphous SiO₂

Experimental evidence shows that both in their crystalline and amorphous states SiO_2 and Si_3N_4 obey Mott's octahedron rule [5]:

Coordination number
$$= 8 - N$$
, (1)

where N is the number of valence electrons.

The valence shell configurations of the silicon, nitrogen, and oxygen atoms are respectively as follows:

Si
$$3s^2 3p^2$$
, N $2s^2 2p^3$, and O $2s^2 2p^4$. (2)

According to rule (1), the silicon, nitrogen, and oxygen atoms are coordinated by four, three, and two atoms, respectively.

 SiO_2 is known to exist in more than ten allotropic modifications, including cristobalite, keatite, coesite, stishovite, the amorphous state, and so forth (see Table 1 below). With the exception of stishovite, with its silicon atom coordinated by six oxygen atoms, in all other modifications the silicon atom possesses a tetrahedral configuration: it is surrounded by four oxygen atoms. Each oxygen atom in a tetrahedral modification links two silicon atoms.

Information about short-range order in SiO₂ is contained in the compound's infrared vibrational spectra. The absorption at a frequency of 1060 cm⁻¹ is mainly due to the valence stretching vibrations of the Si–O bond [6]. For the oxygen atom, this peak is split in two, the high- and low-frequency subpeaks corresponding, respectively, to the antiphase and in-phase displacement of the Si and O atoms. The absorption at 470 cm⁻¹ and the lower-intensity peak at 800 cm⁻¹ are due to the rocking and bending of the Si–O bond, respectively.

As seen in Fig. 1 (taken from Ref. [7]), α -quartz, β -cristobalite, melted quartz, and thermal silicon oxide show several absorption bands in their experimental IR absorption spectra in the frequency range 400–1300 cm⁻¹. The similar vibrational spectra of α -quartz, β -cristobalite, melted quartz, and thermal silicon oxide suggest that it is the short-range ordered atomic arrangement that mainly determines the lattice absorption spectra of the various allotropic modifications of SiO₂. For different crystal modifications of silicon



Figure 1. Infrared absorption spectra of the various allotropic modifications of SiO₂: (a) thermal oxide, (b) melted quartz, (c) β -cristobalite, and (d) α -quartz [7].

dioxide, the refractive index increases with increasing atomic density (Fig. 2).

Table 1. Basic structural parameters of various SiO_2 allotropic forms

Compound Parameter	α-quartz	β-quartz	β-tridymite	α-cristobalite	A-cristobalite	Keatite	Coesite	Stishovite	Glassy structure
Unit cell	Hexagonal	Hexagonal	Hexagonal	Tetragonal	Cubic	Tetragonal	Monoclinic	Tetragonal	_
Number of molecules	3	3	4	4	8	12	16	2	—
Lattice parameters	a = 4.913 c = 5.405	a = 5.01 c = 5.47	a = 5.03 c = 8.22	a = 4.973 c = 6.926	<i>a</i> = 7.16	a = 7.456 c = 8.64	a = 7.17 b = 7.17 c = 12.38 d = 120	a = 4.179 c = 2.665	
Si-O bond length, Å	1.608(2) 1.611(2)	1.616(4)	1.533(2) 1.534 1.562	1.592(2) 1.596	1.609(3) 1.612(1) 1.664(3) 1.649(1)	1.583 1.585 1.605 1.612 1.570 1.612(2)	1.600 1.615 1.611 1.641 1.590 1.612 1.616 1.619		1.62
Si–O–Si angle, degrees	144	146.9	180	148.9	180(4) 137.2(12)	155.8 149.3	180.0(4) 143.5(4) 144.7(8) 139.0(8) 148.2(8)		120-180
Number of bonds in a ring	6	6	6	6	6	5	4		6
Density, g cm ⁻³	2.649	2.352	2.216	2.344	2.174	2.896	2.503	4.287	2.2-2.3



Figure 2. Refractive index versus density for various crystallographic modifications of silicon dioxide: circles and crosses, theory; squares, experiment.

The atomic density radial distribution function (RDF) obtained from X-ray scattering on thermal silicon oxide suggests that the atomic arrangement remains correlated (or short-range ordered) within three coordination spheres. What mainly distinguishes the amorphous state from the crystalline state is a spread in the values of the dihedral Si-O-Si angle, the tetrahedral O-Si-O angle, and the Si-O interatomic distance.

Shown in Fig. 3 is the RDF for thermal SiO₂ obtained by oxidation of silicon in oxygen at 1000 °C. There are four peaks examined experimentally, which can be expanded in terms of pairwise interaction functions. The area under the first peak corresponds to silicon atoms being coordinated tetrahedrally. The atomic density radial distribution functions are similar for melted quartz, dry and wet thermal oxides, and pyrogenic oxide. The basic short-range order characteristics of amorphous SiO₂ are the same no matter how oxides were obtained. The Si–O bond length, O–O distance, and Si–Si distance in SiO₂ are 1.64 Å, 2.63 Å, and 3.10 Å, respectively. The first RDF peak, when approximated by a Gaussian peak, has a dispersion of 0.02 Å. The relative position of the oxygen atoms is characterized by the



Figure 3. Radial distribution function for the atomic density of thermal oxide prepared by silicon oxidation in dry oxygen at 1000 °C.



Figure 4 (a) Fragment consisting of two SiO₂ tetrahedra: Ψ , O–Si–O tetrahedral angle; θ , Si–O–Si dihedral angle. (b) Distribution of O–Si–O tetrahedral angles in dry thermal oxide (*I*), wet thermal oxide (*2*), melted quartz (*3*), and hydrothermal oxide (*4*). (c) Distribution of Si–O–Si dihedral angles in dry thermal oxide (*I*), wet thermal oxide (*2*), melted quartz (*3*,) and hydrothermal oxide (*I*).

value of the O-Si-O tetrahedral angle Ψ (Fig. 4a). The relative position of tetrahedrons is specified by the value of the Si-O-Si dihedral angle θ (Fig. 4a). The average value of 105° found for the O-Si-O tetrahedral angle Ψ in melted quartz, dry and wet thermal oxides, and pyrogenic oxide is close to the value of 109°28′ for an ideal tetrahedron (Fig. 4b). The dihedral angle θ (Si-O-Si) averages in the range of 110°-120° (Fig. 4c). The dihedral angle of SiO₂ fluctuates between 100°-180° (Fig. 4c).

3. Atomic structure of amorphous Si₃N₄

Silicon nitride, when in a crystalline state, exhibits two hexagonal phases, α - and β -Si₃N₄ (Fig. 5), both in the density range 3.1–3.2 g cm⁻³. According to a recent theoretical prediction [8], there also exists a spinel-structured cubic phase, c-Si₃N₄, with a density of 4.0 g cm⁻³. Unlike the hexagonal α - and β -Si₃N₄ phases, a silicon atom in the cubic phase has an octahedral coordination. Also found in the crystalline state is silicon oxynitride Si₂N₂O comprised of SiON₃ tetrahedrons (see Fig. 5).

A comparative look at the lattice reflection spectra of the α -phase of crystalline Si₃N₄ and the transmission spectrum of amorphous Si₃N₄ reveals that the characteristic vibrational modes of crystal and amorphous states are located in nearly the same frequency range (Fig. 6a), implying that the vibrational spectra of both Si₃N₄ and SiO₂ are, to the first approximation, determined by short-range order in the atomic arrangement.

The various methods used in studying short-range order in amorphous Si₃N₄ have produced very similar Si–N bond length values as follows: X-ray diffraction, 1.75 Å; electron diffraction, 1.74–1.75 Å; pulsed neutron scattering, 1.729 \pm \pm 0.05 Å [1], and extended X-ray absorption fine-structure spectroscopy (EXAFS), 1.705 \pm 0.02 Å [9]. As seen in Fig. 6b, the RDF of amorphous Si₃N₄ exhibits three peaks [10]. The radial distribution function has different oscillation amplitudes, depending on the silicon nitride synthesis method. The silicon nitride obtained by pyrolysis — that is, by thermally



Figure 5. Crystal structures of two hexagonal phases of silicon nitride [(a) α -Si₃N₄ and (b) β -Si₃N₄] and (c) silicon oxynitride Si₂N₂O.



Figure 6. (a) Spectral behavior of the reflection coefficient of crystalline α -Si₃N₄ (1) and the transmission spectrum of amorphous Si₃N₄ in the lattice absorption region (2). (b) Radial distribution function for the atomic density of amorphous silicon nitride: 1, plasmochemical nitride, and 2, pyrolytic nitride.

decomposing a mixture of silicon-containing (SiH₄, SiCl₄, SiH₂Cl₂) and nitrogen-containing (NH₃) gases — exhibits more distinct RDF oscillations than its plasmochemical counterpart obtained through the reaction of SiH₄ and NH₃ in a plasma (Fig. 6b). This is a qualitative evidence that the pyrolytic nitride is more ordered. The distribution of N-Si-N tetrahedral angles in the pyrolytic and plasmochemical varieties of silicon nitrides is shown in Fig. 7a taken from Ref. [10]. The tetrahedral angle averages in the range of 115°-125° in both varieties, but has a much narrower distribution in pyrolytic than in plasmochemical silicon nitride. The average value of the Si-N-Si dihedral angle in the pyrolytic and plasmochemical varieties of amorphous Si_3N_4 is close to 120° (Fig. 7b) [10], meaning that, similar to hexagonal crystalline Si₃N₄ of the α and β varieties, a nitrogen atom in amorphous Si₃N₄ lies in the plane of the three neighboring silicon atoms.

4. Atomic structure of silicon oxynitride SiO_xN_y

The chemical composition of silicon oxynitride $\text{SiO}_x N_y$ varies smoothly in going from SiO_2 to $\text{Si}_3 N_4$. The refractive index of $\text{SiO}_x N_y$, measured at a wavelength of 6328 Å, increases from n = 1.46 in SiO_2 to 1.96 in $\text{Si}_3 N4$ (Fig. 8a). Figure 8a also depicts the analytical dependence of the refractive index on the quantity x, a measure of the content of oxygen in silicon oxynitride. These data allow the determination of x using the refractive index measured by ellipsometry. To determine the nitrogen content, the Mott rule [see Eqn (3)] can be applied.



Figure 7. (a) Distribution of N-Si-N tetrahedral angle in amorphous Si_3N_4 obtained by pyrolysis (1) and plasmochemical method (2). (b) The same for Si-N-Si dihedral angle.

The low-frequency dielectric constant of silicon oxynitride varies from $\varepsilon = 3.85$ for SiO₂ to $\varepsilon = 7.0$ for Si₃N₄ (Fig. 8b) [14].

Silicon oxynitride is made up of Si, O, and N atoms and hence contains Si – O and S – N bonds. It is of interest whether SiO_xN_y obeys the Mott rule. Figure 9 displays the X-ray photoelectron spectra of the valence band of silicon oxynitride of various compositions [5]. The valence band of the compound consists of three subbands with ionic gaps inbetween. The 19-eV and 22-eV subbands are mainly due to the N 2s and O 2s electrons. The upper subband at an energy in the range between 0 and 13 eV is formed by O 2p, N 2p, Si 3s, and Si 3p electrons.

If 'ideal' SiO_xN_y compound — that is, one containing only Si-O-Si and Si-N bonds — is described by Mott's rule in terms of its short-range order, then the condition

$$4 = 2x + 3y, \tag{3}$$

should be satisfied, where x and y are the composition parameters of SiO_xN_y . Equation (3) implies that the silicon bonds are equal in number to the nitrogen and oxygen bonds. It is assumed that neither intrinsic ($\equiv Si - Si \equiv$, = N - N =, $\equiv Si^{\bullet} = N_2Si^{\bullet}$, etc.) nor impurity ($\equiv Si_2NH$, $\equiv SiH$) defects are present in any form in silicon oxynitride. The symbols (-) and (•) denote a normal chemical bond and an unpaired electron, respectively.

Figure 10 depicts the dependence of 4/(2x+3y) on x/(x+y) for silicon oxynitride of a variable composition



Figure 8. (a) Refractive index of SiO_xN_y as a function of oxygen content: *I*, taken from Ref. [11]; *2*, from Ref. [12], and *3*, from Ref. [13]. (b) High-frequency dielectric constant as a function of the SiO_xN_y composition: *I*, from capacity measurements in Ref. [14]; *2*, from optical measurements in Ref. [14], and *3*, from Ref. [15].

[5]. The deviation from the Mott rule value of unity is up to 10%. Shown in the same figure is the dependence of 4/(2x + 3y - [NH]) on x/(x + y). Here, [NH] denotes the infrared spectroscopy value for the concentration of hydrogen NH bonds in silicon oxynitride. The last relationship accounts for the presence of nitrogen-bound hydrogen in the compound. The deviation of the last dependence from unity does not exceed 2%, consistent with the accuracy of the X-ray photoelectron spectroscopy used to determine the parameters x and y.

Thus, silicon oxynitride of a variable composition does obey the Mott rule (3). Every silicon atom is coordinated by four nitrogen or oxygen atoms, an oxygen atom — similar to what occurs in silicon dioxide — is linked to two silicon atoms, and a nitrogen atom — similar to what occurs in silicon nitride — is coordinated by three nitrogen or hydrogen atoms.

Using the Mott rule, the definition of a defect in a tetrahedral amorphous solid can be formulated as follows [5]: a point defect is any deviation — either in terms of the Mott rule coordination number or in terms of atomic species — away from the ideal defect-free structure. In the case of silicon oxynitride SiO_xN_y , the defects covered by this definition are the following: paramagnetic (\equiv Si•, \equiv Si•+Si \equiv , \equiv Si₂N•, \equiv SiO•, \equiv SiOO•), diamagnetic (= N-N =, \equiv Si-Si \equiv , = Si²NH, \equiv SiH), neutral



Figure 9. X-ray photoelectron spectra of the SiO_xN_y valence band. The top of the Si_3N_4 valence band is taken as the zero energy point.



Figure 10. Number ratio of silicon bonds to oxygen and nitrogen bonds in SiO_xN_y .

 $(\equiv Si-Si \equiv, = N-N =, \equiv SiH, \equiv Si_2N_{\bullet}, = Si^{\bullet})$, charged $(\equiv Si_{\bullet}+Si \equiv, \equiv SiO^{\bullet})$, intrinsic $(= N_2Si_{\bullet}, \equiv Si-Si \equiv, \equiv SiOOS \equiv)$, and impurity $(\equiv Si_2NH, \equiv SiH, \equiv SiOH)$.

There are two models available to describe the structure of the tetrahedral SiO_xN_y , $SiN_{x<4/3}$, and $SiO_{x<2}$ compounds [1, 16]. One, the random mixture (RM) model, assumes that silicon oxynitride consists of two kinds of tetrahedrons: SiO_4 and SiN_4 . SiO_xN_y in this case consists of two phases, SiO_2 and Si_3N_4 . In the random bonding (RB) model, SiO_xN_y is assumed to consist of five kinds of tetrahedrons, described



Figure 11. Probability of finding $\text{SiO}_v \text{N}_{4-v}$ tetrahedron in $\text{SiO}_x \text{N}_y$, SiO_vSi_{4-v} tetrahedron in SiO_x, and SiN_vSi_{4-v} tetrahedron in SiN_x. For SiO_x, $\delta = x/2$; for SiN_x, $\delta = x/3$, and for SiO_xN_v, $\delta = 3x/(3x + 2y)$.



Figure 12. Infrared absorption spectra of silicon oxynitride of a variable composition: $1 - \text{Si}_3\text{N}_4$, $2 - \text{Si}O_x\text{N}_y$, and $3 - \text{Si}O_2$.

by the generic formula $\text{SiO}_{\nu}N_{4-\nu}$, $\nu = 0, 1, 2, 3, 4$ (SiN₄, SiON₃, SiO₂N₂, SiO₃N, SiO₄). The probability of finding an SiO_{ν}N_{4- ν} tetrahedron depends on the chemical composition of the compound (Fig. 11). Figure 12 presents the lattice absorption spectra of silicon oxynitride of different compositions. The absorption peak shifts monotonically to higher vibration frequencies with increasing oxygen content, thus qualitatively supporting the **RB** model.

Similar behavior is seen in X-ray photoelectron spectra. Figure 13 displays the photoelectron spectra from the Si 2p atomic levels in SiO_xN_y of a variable composition [17, 18]. Increasing oxygen content in silicon oxynitride makes the Si 2p peak shift to higher binding energies. The single-peak behavior is an argument in favor of the RB model.

Figure 13 also presents the photoelectron spectrum of $SiO_{1.26}N_{0.57}$ calculated using the RM model. The spectrum shows two peaks, one corresponding to SiO_2 and the other to Si_3N_4 , and disagrees with experiment.

For RB-structured amorphous silicon oxynitride, the distribution function of $SiO_x N_y$ tetrahedra in $SiO_y N_{4-y}$ is given by the expression (see Fig. 11)

$$W(v, x, y) = \left(\frac{2x}{2x+3y}\right)^{\nu} \left(\frac{3y}{2x+3y}\right)^{4-\nu} \frac{4!}{\nu!(4-\nu)!} .$$
 (4)



Figure 13. X-ray photoelectron spectra from Si 2p atomic levels in $SiO_x N_y$ of a variable composition.



Figure 14. Energies of Si 2p, N 1s, and O 1s atomic levels in $SiO_x N_y$ of a variable composition.



Figure 15. Energies of the Si 2p, N 1s, and O 1s atomic levels in SiO_xN_y of a variable composition as a function of the Hasegawa-model-calculated effective charge [16].

Expression (4) implies that the SiO_xN_y compound consists only of Si–O and Si–N bonds and contains no intrinsic or impurity defects. Figure 13 presents the photoelectron spectra of silicon oxynitride calculated under the assumption that its structure is described by the RB model. The experimental photoelectron spectra are well described by the RB model for a wide range of oxynitride compositions, from SiO₂ to Si₃N₄. The smooth chemical shift of the O 1s, N 1s, and Si 2p levels provides further experimental evidence to favor RB as a structure model for SiO_xN_y (Fig. 14). Shown in Fig. 15 is the position of the atomic levels of SiO_xN_y as a function of the Hasegawa-model-calculated effective charge [16].

Thus, the random bonding model is quite adequate to quantitatively describe the structure of amorphous silicon oxynitride over a wide range of compositions.

5. Atomic structure of nonstoichiometric silicon oxide SiO_x

The refractive index of SiO_x decreases with decreasing oxygen content due to an increase in the concentration of Si–O bonds. The structure of SiO_x, as opposed to SiO_xN_y, fails to be described by the RM model. For the RM model, the distribution function of SiO_ySi_{4-v} tetrahedra, v = 0, 1, 2, 3, 4



Figure 16. X-ray photoelectron spectra of Si 2p atomic levels in SiO_x .

in SiO_x is given by the expression (see Fig. 11)

$$W(\nu, x) = \left(\frac{x}{2}\right)^{\nu} \left(1 - \frac{x}{2}\right)^{4-\nu} \frac{4!}{\nu!(4-\nu)!} .$$
 (6)

Figure 16 displays the photoelectron spectra of the Si 1p levels in SiO_x of different compositions prepared by oxidizing silane SiH₄ in oxygen at 700 °C [19]. The two peaks observed, one corresponding to SiO₂ and the other to Si, suggest that RM provides a good first approximation to the structure of SiO_x. However, there is also experimental evidence for SiOSi₃, SiO₂Si₂, SiO₃Si tetrahedra. Reference [19] discusses a model involving large-scale potential fluctuations due to local chemical composition fluctuations of silicon oxide (SiO_x). Notably, the structure of SiO_x depends on exactly how the oxide was made. For example, SiO_x films obtained by sputtering silicon in oxygen at low temperatures do not decompose into an SiO₂ phase and an Si phase [20].

6. Atomic structure of Si-rich silicon nitride SiN_x

The refractive index of SiN_x increases as the excess silicon content increases (see Fig. 17 taken from Ref. [21]). The density and concentration of silicon and nitrogen atoms as determined from Rutherford scattering data are shown in Fig. 18 (taken from Ref. [21]) as a function of the SiN_x composition. Increasing the excess silicon content in SiN_x decreases the energy of plasmons, i.e., of valence electron oscillations (from 24.0 eV in Si_3N_4 to 17.0 eV in Si). The



Figure 17. Refractive index as a function of SiN_x composition: *1*, from Ref. [22]; *2*, from Ref. [23], and *3*, from Ref. [21].



Figure 18. Absolute concentrations of silicon and nitrogen atoms and density as a function of SiN_x composition: *1*, from Ref. [22]; *2*, from Ref. [23], and *3*, from Ref. [21].

silicon nitride deposition due to the decomposition of silane (SiH_4) and ammonia (NH_3) in plasma allows the synthesis temperature to be reduced to between 250 and 500 °C, with the resulting nitride showing higher concentrations of Si-H and N-H hydrogen bonds. This nitride has a chemical formula of SiN_x•H. The latter compound, in addition to



Figure 19. X-ray photoelectron spectra from Si 2p atomic levels in SiN_x .

Si-N, Si-H, and N-H bonds, has Si-Si bonds (implying excess silicon). This means that the parameter x < 4/3 in this nitride. A point of interest is whether the Mott octahedral rule is a good description of the compound's structure. Reference [24] shows that a nitrogen atom in SiN_x H is coordinated by three silicon and hydrogen atoms, whereas a silicon atom is coordinated by four silicon and hydrogen atoms. Thus, the coordination of silicon and nitrogen atoms in SiN_x H is described quantitatively by the Mott rule (1).

In contrast to silicon oxynitride, the structure of siliconrich SiN_x cannot be described by the RB model (see Fig. 19 taken from Ref. [18]). In the case in which the structure of SiN_x is described by the RB model, the distribution function of SiN_vSi_{4-v} tetrahedra, v = 0, 1, 2, 3, 4 (SiN₄, SiNSi₃, SiN₂Si₂, SiN₃Si, SiSi₄) can be expressed as (see Fig. 11)

$$W(\nu, x) = \left(\frac{3x}{4}\right)^{\nu} \left(1 - \frac{3x}{4}\right)^{4-\nu} \frac{4!}{\nu!(4-\nu)!} .$$
 (5)

The RB-model photoelectron spectrum exhibits a single peak which shifts to higher energies as the nitrogen content in SiN_x increases (see Fig. 19). In the RM model, the photoelectron spectrum has two peaks whose amplitude ratio depends on the silicon nitride composition. The experimental photoelectron spectra of SiN_x exhibit a peak and a shoulder at the respective energies corresponding to Si₃N₄ and Si. The SiN_x compound is made up of SiN₄, SiSiN₃, SiSi₂N₂, SiSi₃N, and SiN₄ tetrahedra, but their distribution function is not described by expression (5). The ion bombardment of the SiN_x compound results in a narrower photoelectron spectrum and produces a single peak. The structure of irradiated SiN_x is qualitatively described by the RB model. The Raman spectra of SiN_x show a peak whose energy shifts to lower frequencies as the silicon content is increased. This peak is due to the presence of silicon clusters in SiN_x . Using the Raman scattering and photoluminescence methods, clusters of amorphous silicon have been observed in SiN_x [25–27].

The SiN_x structure shown in a two-dimensional schematic in Fig. 20 involves the presence of three phases: silicon nitride, amorphous silicon, and silicon subnitrides. At the bottom of Fig. 20a is shown a one-dimensional energy diagram illustrating the large-scale potential fluctuations in SiN_x [18]. The respective band gaps of amorphous silicon and Si₃N₄ are 1.6 eV [27] and 4.5 eV [28]. The energy barrier for holes at the Si/Si₃N₄ interface amounts to 1.5 eV [28, 29], leading to a value of 1.5 eV for the barrier for electrons there. A local fluctuation in the chemical composition x in SiN_x causes a local change in the band gap (Fig. 20a). Figure 20b shows for comparison the Shklovskii-Efros potential fluctuation model for a highly doped compensated semiconductor [30]. Potential fluctuations in a compensated semiconductor are due to the nonuniform distribution of charged (ionized) donors and acceptors. When an electron – hole pair is excited in a compensated semiconductor, an electric field tends to separate the electron and the hole spatially. In SiN_x , what a local electric field does in this case is to localize the electron and the hole at the same point in space, thus causing the two to recombine.



Figure 20. Model of large-scale potential fluctuations in SiN_x: χ , electron affinity; Φ_e and Φ_h , potential fluctuation scales of electrons and holes, respectively; E_c , E_v , and μ , positions of the conduction band bottom, valence band top, and the Fermi level, respectively.

7. Conclusions

This review summarizes the current knowledge of the atomic structure of nonstoichiometric silicon oxides and nitrides of varying compositions. In recent years, considerable progress in understanding the structure of these materials has been achieved using high-resolution photoelectron spectroscopy in general, and synchrotron radiation in particular.

A well-established finding of the last decade is that shortrange order in the oxides and nitrides of silicon is determined by short-range order in atomic arrangement. It has been shown that amorphous silicon oxynitride (SiO_xN_y) and the silicon-rich nitride (SiN_x) have their short-range order determined by the Mott octahedral rule in a wide range of compositions, from SiO₂ to Si₃N₄ and from Si₃N₄ to Si, respectively. This means that a silicon atom is, as in the case of silicon, coordinated by four atoms of oxygen and/or nitrogen; an oxygen atom is (as in SiO₂) coordinated by two silicon atoms, and a nitrogen atom is (as in Si₃N₄) coordinated by three silicon atoms. Based on the Mott rule, a definition of a defect in the amorphous state was formulated.

The structure of amorphous silicon oxynitride is quantitatively explained by the random bonding model over a wide range of compositions. According to this model, silicon oxynitride is made up of five kinds of tetrahedra in which oxygen and nitrogen atoms substitute randomly for one another. In contrast to oxynitride, the structures of nonstoichiometric silicon oxide (SiO_{x<2}) and silicon nitride (SiN_{x<4/3}) are not described by the RB model. Nor does the other extreme approach, the random mixture model, provide a quantitative description of the structure of these materials, despite the phase decomposition they tend to exhibit (into Si and SiO₂ in SiO_x, and into Si and Si₃N₄ in SiN_x). In the proposed intermediate structure model, SiN_x and SiO_x are made up of five kinds of tetrahedra, but their distribution statistics are not described by random laws.

Based on the intermediate model, a model of large-scale potential fluctuations is suggested for SiN_x and SiO_x . In this, local spatial fluctuations in chemical composition lead to contravariant (counterphase) potential fluctuations for electrons and holes. This model differs fundamentally from Shklovskii and Efros's scenario of large-scale potential fluctuations in a heavily doped compensated semiconductor, in which potential fluctuations are due to the nonuniform distribution of charged donors and acceptors. The potentials for electrons and holes fluctuate in phase in the Shklovskii – Efros model.

Currently, the Si/SiO₂ interface is the most studied among solid state interfaces. Photoelectric spectroscopy studies of this interface using synchrotron radiation have provided conclusive evidence of the existence of excessive, superstoichiometric silicon near the interface in the oxide. However, the experimental fact that the refractive index of thermal silicon oxide decreases with an increase in thickness can be explained by assuming that this effect is due to a change in the number of Si–O bonds in a closed ring over the thickness of SiO₂. The question remains open whether excessive silicon can account for the fact that the refractive index of oxide decreases as its thickness increases.

It was established that nitrogenizing thermal oxide leads, as a result of the nitrogen interaction with the excessive silicon, to the removal of silicon-silicon bonds, an effect which is used to decrease the concentration of hole traps in a dielectric. The appearance of excessive silicon due to the oxidation of silicon nitride explains the accumulation of excessive charge in silicon-nitride-based memory devices. The nature of the traps responsible for the localization of electrons and holes in silicon nitride is yet to be understood in terms of the atomic and electronic structure.

Acknowledgments. This work has been supported by the SB RAS integrational project No. 97 and by RFBR grant No. 01-02-16621.

References

- Gritsenko V A Atomnaya i Elektronnaya Struktura Amorfnykh Dielektrikov v Kremnievykh MDP Strukturakh (Atomic and Electronic Structure of Amorphous Dielectrics in Silicon MIS Structures) (Novosibirsk: Nauka, 1992)
- Gritsenko V A, in *Silicon Nitride in Electronics* (Materials Science Monographs, Vol. 34, Ed. A V Rzhanov) (New York: Elsevier, 1988)
- 3. She M, Takeuchi H, King T-J *IEEE Electron Device Lett.* **24** 309 (2003)
- 4. Gritsenko V A et al. Solid-State Electron. 47 1651 (2003)
- 5. Gritsenko V A et al. Phys. Rev. Lett. 81 1054 (1998)
- 6. Pai P G et al. J. Vac. Sci. Technol. A **4** 689 (1986)
- 7. Nagasima N et al. Jpn. J. Appl. Phys. 9 879 (1986)
- 8. Mo S-D Phys. Rev. Lett. 83 5046 (1999)
- 9. Stöhr J et al. Phys. Rev. B 20 664 (1979)
- Repnikova E A, Gurtov V A, Panova Z V Phys. Status Solidi A 119 113 (1990)
- 11. Kuiper A E T et al. J. Vac. Sci. Technol. B 1 62 (1983)
- 12. Rand M, Roberts J F J. Electrochem. Soc. 120 446 (1973)
- Gritsenko V A "Sostav, stroenie, elektronnaya struktura i perenos zaryada v amorfnom oksinitride kremniya" ("Composition, Structure, Electronic Structure and Charge Transfer in Amorphous Silicon Oxynitride"), Preprint No. 5 (Novosibirsk: Institute of Semiconductor Physics, Siberian Branch of the USSR Acad. of Sci., 1985)
- 14. Eriksson T S, Granqvist C G J. Appl. Phys. 60 2081 (1986)
- 15. Brown D M et al. J. Electrochem. Soc. 115 311 (1968)
- 16. Hasegawa S et al. Phys. Rev. B 46 12478 (1992)
- 17. Gritsenko V A et al. Philos. Mag. B 80 1857 (2000)
- 18. Gritsenko V A et al. J. Non-Cryst. Solids 297 96 (2002)
- Gritsenko V A, Kostikov Yu P, Romanov N A Pis'ma Zh. Eksp. Teor. Fiz. 34 6 (1981) [JETP Lett. 34 3 (1981)]
- 20. Bell F G, Ley L Phys. Rev. B 37 8383 (1988)
- 21. Bolotin V P et al. Dokl. Akad. Nauk SSSR 310 114 (1990)
- 22. Gyulay J et al. J. Appl. Phys. 42 451 (1971)
- 23. Makino T K J. Electrochem. Soc. **130** 450 (1983)
- 24. Nakahiro V, Masashiko M Jpn. J. Appl. Phys. 13 1300 (1986)
- 25. Volodin V A et al. Appl. Phys. Lett. 73 1212 (1998)
- 26. Molinari M, Rinnert H, Vergnat M Appl. Phys. Lett. 77 3499 (2000)
- 27. Park N-M et al. Phys. Rev. Lett. 86 1355 (2001)
- 28. Gritsenko V A, Meerson E E, Morokov Yu N Phys. Rev. B 57
 - R2081 (1998)
- 29. Gritsenko V A et al. *Thin Solid Films* **437** 135 (2003)
- Shklovskii B I, Efros A L Elektronnye Svoistva Legirovannykh Poluprovodnikov (Electronic Properties of Doped Semiconductors) (Moscow: Nauka, 1979) [Translated into English (Berlin: Springer-Verlag, 1984)]