Electronic structure of silicon oxynitride: Ab-initio and experimental study, comparison with silicon nitride

S. S. Nekrashevich and V. A. Gritsenko
A.V. Rzhanov Institute of Semiconductor Physics SB RAS, 630090 Novosibirsk, Russia

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Amorphous silicon oxide SiO₂, silicon nitride Si₃N₄, and silicon oxynitride SiOₓNₓ are three key dielectrics in silicon devices. Implementation of nitrided oxide (oxynitride SiOₓNₓ) as a gate dielectric in metal-oxide-semiconductor field effect transistors has been shown to significantly improve the reliability and lifetime of devices. Also, amorphous oxynitride is used as a tunnel dielectric in nonvolatile flash memory devices. The present paper is devoted to the experimental and theoretical study of silicon oxynitride electronic structure. The ionic formula of crystalline Si₂N₂O is deduced from the first principles. Effective masses of charge carriers in Si₂N₂O are calculated and compared with experimental data on tunnel injection in amorphous SiNₓO₁₋ₓ samples. Also experimental x-ray absorption and emission spectra are compared with the theoretically calculated ones. © 2011 American Institute of Physics. [doi:10.1063/1.3653833]

I. INTRODUCTION

Amorphous silicon oxide SiO₂, silicon nitride Si₃N₄, and silicon oxynitride SiOₓNₓ are three key dielectrics in silicon devices. Silicon oxide has been used as a gate dielectric in metal-oxide-silicon (MOS) devices for more than four decades. Aggressive scaling of MOS devices is accompanied by gate SiO₂ thickness decreasing to 1.0–1.5 nm. In such devices, the direct tunnel current results in high power dissipation. Now in power devices, SiO₂ is being replaced by high-k dielectrics. High dielectric permittivity increases physical thickness to ≈5 nm and by this way suppresses tunnel current. However, application of high-k dielectrics does not make use of SiO₂ and SiOₓNₓ impossible. For generating high quality silicon/insulator structure, the interface of SiO₂ or SiOₓNₓ with thickness about 0.5 nm is usually grown between silicon and high-k dielectric.

In low power logic devices, SiO₂ is now being replaced by middle-k dielectric SiOₓNₓ. Silicon oxynitride will be used as a gate dielectric in logic devices up to year 2016. Implementation of nitrided oxide (oxynitride SiOₓNₓ) as a gate dielectric in metal-oxide-semiconductor field effect transistors (MOSFETs) has been shown to significantly improve the reliability and lifetime of devices due to the suppression of impurities diffusion, decreased charge trapping in the dielectric, less stress induced leakage current, suppression of interface states generation, and higher tolerance to radiation. Also amorphous oxynitride is used as a tunnel dielectric in nonvolatile flash memory devices.

The amorphous SiOₓNₓ has excellent optical properties, such as low absorption losses in the visible and near infrared wavelength range. The gap of SiOₓNₓ changes in the range of 4.5–8.0 eV. Moreover, the refractive index of SiOₓNₓ thin films can be easily adjusted over a large range between 1.46(SiO₂) and 1.96(Si₃N₄). This large flexibility in choosing the refractive index adds to the attractiveness of this material for the design of integrated optical devices, particularly in waveguiding structures in optical communication or anti-reflective and coating layers.

Crystalline silicon oxynitride Si₂N₂O consists of tetrahedrons SiN₄, where nitrogen atom is coordinated by three silicon atoms and oxygen atom is coordinated by two silicon atoms. The electronic structure of crystalline silicon oxynitride Si₂N₂O was studied in Ref. 9. The band calculations of Si₂N₂O were reported in Refs. 10 and 11. In Ref. 11, the ionic formula of crystalline silicon oxynitride (Si₁₋₂.₅₄)(N₁₋₁.₈₉)₂(O₁₋₁.₂₅) was calculated. The ionic formula of silicon nitride calculated in the same paper was x(Si₁₋₂.₅₂)(N₁₋₁.₈₉)₄. Thus, the theoretically predicted charge transfer on Si-N bond is ΔQ = 0.63e. However, the experimentally obtained ionic formula of amorphous Si₂N₂O is (Si₁₋₁.₄₂)(N₁₋₁.₀₅)₄. The experimental value of charge transfer on Si-N bond is ΔQ = 0.35e. Thus, the calculation in Ref. 11 overestimates the Si-N bond charge transfer almost by the factor of 2. For that matter, it is reasonable to assume that the ionic formula of Si₂N₂O is also incorrect. Amorphous oxinitride a-SiOₓNₓ consists of Si-O and Si-N bonds which create five sorts of tetrahedron Si₂O₃Nₓ, ν = 0,1,2,3,4. The experimental study of electronic structure of amorphous Si₂N₂O by means of x-ray emission spectroscopy was conducted in Ref. 13. Experimental results of photoelectron spectroscopy are given in Ref. 14.

II. EXPERIMENTAL METHODS FOR ELECTRONIC STRUCTURE STUDY OF SOLIDS

The experiment is based on the registration of emission spectra caused by the transition of valence electrons to vacant core levels Si 1s, Si 2p, N 1s, O1s (Fig. 1). X-ray emission intensity is proportional to the electronic density of states in the valence band. The valence band width of Si₂N₂O is about 13 eV, which is significantly lower than the energy of roentgen transitions observed in the emission spectra. For that matter, it is assumed that the transition matrix element has weak correlation with transition energy. In the dipole approximation, the only roentgen transitions...
allowed are those where orbital moment is changed at \( \pm 1 \). According to the dipole selection rules, in Si L\(_{2,3}\) emission spectra transitions from Si 3s, 3d states of valence band to the Si 2p core level occur. In the Si K emission spectra, transitions from Si 3p to Si 1s level are registered. In the N K and O K emission spectra transitions from 2p states of valence band to N 1s and O 1s states, respectively, are registered. The density of states in the conduction band is studied in experiments on x-ray absorption spectra or quantum efficiency spectra. In quantum efficiency, spectra transitions from filled Si 1s, Si 2p, N 1s, O 1s states to unpopulated levels of conduction band are observed. Quantum efficiency spectra are interpreted in terms of dipole selection rules.

### III. CALCULATION OF THE IONIC FORMULA

Energies of the atomic levels (i.e., the position of Si 2p level in the tetrahedral solids like Si, Si\(_3\)N\(_4\), SiO\(_2\)) are determined by the values of effective charges on silicon atoms which, in turn, are determined by electron affinity of the atoms surrounding a silicon atom. Such a physical value as atom effective charge does not have strictly defined rules of calculation. However, comparison of atom charges for different compositions makes the estimation of wavefunctions overlap and also charge transfer per bond possible. Difference between Si 2p levels of Si\(_3\)N\(_4\) and Si is 2.9 eV and of SiO\(_2\) and Si is 4.2 eV.\(^{12}\) This difference (chemical shift) is caused by the shifting of electron shell from s- and p- levels of silicon atom to 2p levels of nitrogen or oxygen atoms after the formation of Si-N and Si-O bonds. For that reason, the silicon atom is charged positively, nitrogen and oxygen atoms are charged negatively. Due to the positive charge on silicon atom in Si\(_3\)N\(_4\), SiO\(_x\)N\(_y\), and SiO\(_2\), Si-2p level energy raises because of Coulomb interaction. That is the essence of Si-2p level chemical shift in Si\(_3\)N\(_4\), SiO\(_x\)N\(_y\), and SiO\(_2\).

The charge on the oxygen atom in melted quartz was obtained from experiments on positron annihilation and had the value of \( Q^O = -1.0e \).\(^{16}\) Theoretical quantum-chemical calculations of the SiO\(_2\) electronic structure give a similar result: 1.2e,\(^{17}\) 1.02-1.3e,\(^{18}\) 1.15e,\(^{19}\) 1.2e.\(^{20}\) Since the oxygen atom in SiO\(_2\) is twofold coordinated by silicon atoms, the charge transfer on Si-O bond is \( \Delta Q = 0.5e \). It means that SiO\(_2\) is ionic-covalent solid with a large part of ionicity of the Si-O bond.

The charge transfer on the Si-N bond in Si\(_3\)N\(_4\) can be calculated from the chemical shift. The Si-Si bond is covalent, so the Si atom in silicon is neutral (\( Q_{Si} = 0 \)). Assuming that the chemical shift is proportional to the positive charge on the Si atom, the effective charge of Si in Si\(_3\)N\(_4\) is \( Q_{Si} = +1.4e \).\(^{12}\) Since the silicon atom in Si\(_3\)N\(_4\) is fourfold coordinated by nitrogen atoms, the charge transfer per Si-N bond is \( \Delta Q = 0.35e \). The nitrogen atom in Si\(_3\)N\(_4\) is threefold coordinated, so the nitrogen atom charge is \( Q^N = -1.05e \). And, thus, the ionic formula of amorphous silicon nitride is \((Si^{+1.4})_3(N^{-1.05})_4\).

The SiO\(_{0.56}N_{1.6}\) formula is close to Si\(_2\)N\(_2\)O. We assume that the silicon atom charge in Si\(_2\)N\(_2\)O is the same as in Si\(_3\)N\(_4\) and so is the Si-N bond charge transfer. Since the silicon atom in Si\(_2\)N\(_2\)O is coordinated by three nitrogen atoms and one oxygen atom, Si atoms charge is \( Q^O = +0.35 \times 3 + 0.5 \times 1 \) = +1.55e. So the full estimated ionic formula of crystalline Si\(_2\)N\(_2\)O obtained from experiment is \((Si^{+1.55})_2(N^{-1.05})_2(O^{-1.0})\).

The charge of silicon atom theoretically calculated in the
The present work is \( \text{QSi} = 1.6 \) and the full ionic formula is \((\text{Si}^{1.6})_2(\text{N}^{1.04})_2\text{O}^{-0.8}\).

## IV. THEORETICAL MODEL

The \( \text{Si}_2\text{N}_2\text{O} \) primitive unit cell contains 20 atoms and has an orthorhombic syngony \((a = 8.8717(6) \ \text{Å}, b = 5.4909(16) \ \text{Å}, c = 4.8504(7) \ \text{Å})\), Fig. 2. In the same figure, the first Brillouin zone is shown. Calculations of electronic structure were conducted in the QUANTUM-ESPRESSO software package which employs DFT framework with a plane-wave basis set, pseudopotentials, and periodic boundary conditions.

For the atoms involved in our calculations, the following electronic configurations were used—\( \text{Si}: [\text{Ne}] \ 3s^2 \ 3p^2 \ 3d^5 \), \( \text{N}: [\text{He}] \ 2s^2 \ 2p^3 \), \( \text{O}: [\text{He}] \ 2s^2 \ 2p^4 \). Core states were considered using ultrasoft Vanderbilt pseudopotentials.

The plane-waves cut-off energy was chosen so that the total supercell energy convergence was not worse than 0.001 Ry/atom and was equal 45 Ry. K-points grid density in reciprocal space was chosen the same way. Holes and electrons effective masses were estimated from the calculated dispersion \( E(k) \), approximating the dispersion law with parabola in the vicinity of local extreme points.

## V. BAND STRUCTURE AND EFFECTIVE MASSES

Tunnel leakage current of silicon oxinitride is defined by the energy barrier on the \( \text{Si}/\text{SiO}_x\text{N}_y \) interface and by effective masses of charge carriers.\(^{21,22} \) Effective masses calculated from the dispersion law (Fig. 3) in comparison with effective masses for silicon nitride, results of theoretical calculation in Ref. 10, and experiments on tunnel injection of carriers\(^{23} \) are given in the Table I. Just like in Ref. 11, the effective mass of electron \((0.4m_0)\) well agrees with the experimental value of the electronic tunnel effective mass obtained in experiments on amorphous samples of \( \text{SiO}_x\text{N}_y \) \(0.21–0.5 \ m_0 \).\(^{23} \) However, there is a discrepancy in theoretical value obtained in our simulation \((1.0m_0)\) and experimental \((0.4m_0)\) values of holes effective masses in \( \text{Si}_2\text{N}_2\text{O} \).\(^{22} \) For silicon nitride, both electron and hole effective masses well agree with experiment.\(^{24} \)

The calculation of the band structure has shown that crystalline \( \text{Si}_2\text{N}_2\text{O} \) is a direct-gap insulator with the top of the valence band and the bottom of the conduction band in the center of Brillouin zone (G-point). The calculated bandgap value is 5.1 eV which is close to the experimental bandgap energy for amorphous silicon oxynitride of the composition close to \( \text{Si}_2\text{N}_2\text{O} – 5.3 \ \text{eV} \).\(^{8,12} \)

## VI. PARTIAL DENSITY OF STATES IN SILICON OXYNITRIDE AND NITRIDE

More detailed information on electronic structure of silicon oxynitride can be obtained from experiments on x-ray

![Si2N2O bandstructure](image_link)
emission and quantum yield spectra and its comparison with the calculated partial density of electronic states (Fig. 4). Si L_{2,3} x-ray emission and quantum yield spectra are contributed by Si 3s and Si 3d states. But, in the present work, there are no 3d states in the basis. Consideration of these states leads to a high-energy peak near the top of the valence band.\textsuperscript{11} Si 3d states also contribute to electronic states in the top of the valence band in SiO\textsubscript{2} and Si\textsubscript{3}N\textsubscript{4}.\textsuperscript{25} Fig. 5 shows the similar data for silicon nitride. It can be noticed that all major features of the Si\textsubscript{3}N\textsubscript{4} spectra are reproduced in silicon oxynitride.

Experiment and simulation showed that silicon oxynitride valence band consists of three subbands. The deepest one (≈20 eV) is formed by 2s states of oxygen and the second one (≈14 eV) is formed by 2s states of nitrogen. The top valence subband is formed by (in the order from top of the valence band down to subband bottom) N 2p\textsubscript{z}, O 2p\textsubscript{z} non-bonding and bonding N 2p, O 2p, Si 3s,p,d orbitals.

This interpretation is based on the analysis of the spatial charge distribution of different energy levels on Si, N, and O atoms (Figs. 6(a)–(d)). Within the energies about –18 eV and –14 eV, the simulation showed a spherically symmetric charge distribution on oxygen and nitrogen atoms corresponding to the s-symmetry of wavefunctions (Figs. 6(a) and

### Table I. Effective masses of charge carriers in Si\textsubscript{2}N\textsubscript{2}O and Si\textsubscript{3}N\textsubscript{4}.

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<th>Si\textsubscript{2}N\textsubscript{2}O</th>
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<td>DFT simulation (Omr)</td>
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FIG. 4. Experimental x-ray emission and absorption spectra of SiO\textsubscript{0.56}N\textsubscript{1.06} (solid black curve) in comparison with partial density of states of Si\textsubscript{2}N\textsubscript{2}O (thin gray curve).

FIG. 5. Experimental x-ray emission and absorption spectra (solid curve) in comparison with partial density of states of Si\textsubscript{3}N\textsubscript{4} (dotted curve).
The bottom of the upper valence band shows charge concentration on the p-states of oxygen and nitrogen atoms, even though they are hybridized with Si 3s, 3p, 3d levels, forming bonding states (Fig. 6(c)). Localization of the charge on the oxygen and nitrogen atoms proves that Si-N and Si-O bonds are ionic ones. On the very top of the valence band, non-bonding O 2p\textsubscript{z} and N 2p\textsubscript{z} states are localized. That follows from the distribution of electronic density which is localized in the direction normal to Si-N and Si-O bonds (Figs. 6(d) and 6(e)).

Si 3p states contribute to the Si K spectra. These states make maximal contribution near the middle of the upper valence subband. It is important to notice that Si 3p states also contribute to the upper part of the valence band where O 2p\textsubscript{z} and N 2p\textsubscript{z} dominate.

O K and N K x-ray emission spectra are formed by O 2p and N 2p bonding orbitals and O 2p\textsubscript{z} and N 2p\textsubscript{z} nonbonding orbitals. Fig. 1 shows the scheme of roentgen transitions in SiO\textsubscript{0.56}N\textsubscript{1.06}. This scheme is deduced empirically on the analogy with SiO\textsubscript{2}.26

VII. PHOTOELECTRON SPECTRA OF SiO\textsubscript{x}N\textsubscript{y} VALENCE BAND

Roentgen photoelectron spectra of the amorphous SiO\textsubscript{x}N\textsubscript{y} of variable composition were studied in Ref. 14. Comparison of these experimental spectra with the theoretically predicted ones is given in Fig. 7. The calculation was made as follows. First, the partial density of states for crystalline Si\textsubscript{2}N\textsubscript{2}O had been calculated. After that, s- and p- spectra of each atom sort were multiplied by the corresponding ionization cross-section\textsuperscript{27} and the coefficient corresponding to the concentration of the considered atom sort in the given composition of the SiO\textsubscript{x}N\textsubscript{y}.

It can be noticed that the experiment and calculation are in good qualitative agreement. For example, in both experimental spectra and calculation, the bottom peak corresponding to the O 1s states reduces, while the second peak
corresponding to the N 1s states increases as the composition changes from SiN_{0.57}O_{1.26} to SiN_{1.30}O_{0.23}.

VIII. DISCUSSION AND CONCLUSION

The experimentally obtained Si-N charge transfer value in the Si3N4 bond, \( \Delta Q = 0.35 \text{e} \), is twice less than the value of 0.7e calculated in Ref. 11. The Lowden atomic charges calculated in the present paper (\( Q_{\text{Si}} = +1.6 \text{e}, Q_{\text{N}} = -1.04 \text{e}, Q_{\text{O}} = -0.8e \)) also made the calculation of the charge transfer for Si-N: \( \Delta Q = 0.34 \pm 0.02 \text{e} \) and Si-O: \( 0.4 \pm 0.05 \text{e} \) bonds possible.

DFT calculations show that non-bonding O 2p orbitals in SiO2 form a narrow band at the top of the valence band.17 This band is separated from the bonding orbitals by \( \approx 1 \text{ eV} \) wide gap. It should be noticed that cluster calculations do not predict that gap in the SiO2.28 Experiments in photoelectron and x-ray emission spectroscopy do not reveal that gap either.

On the top of the valence band of the silicon nitride, there are also non-bonding N-2p orbitals. However, neither DFT calculations nor experiment predicts the gap between N 2p and N 2p, Si-3s,p,d states.7,11 Whence, it follows that the electronic structure of Si2N2O is more similar to the one of Si3N4, than SiO2.

We also want to emphasize that, in the present work, the comparison between calculations of the crystalline Si3N4 formed by SiN4 tetrahedron and experimental data on amorphous \( \text{SiO}_{0.56}\text{N}_{1.06} \) formed by five sorts of \( \text{SiO}_{3n}\text{N}_{4-n} \) tetrahedron (\( \nu = 0,1,2,3,4 \)) is given. Nevertheless, calculation and experimental data are in a good agreement. This fact proves that the major features of solids electronic structure are determined by a short-range order of the atomic structure.

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