

Electronic structure of amorphous silicon oxynitride with different compositions

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A revised tight-binding Hamiltonian parametrization scheme for calculating the electronic structure of both covalent and ion-covalent solids is proposed. Unlike the conventional approaches, the present nonempirical calculation does not rely on any empirical parameter. We use the atomic properties of isolated atoms to construct the matrix elements. Results show that the predicted charge transfer in SiO₂ and Si₃N₄, the bandgap energies of SiO₂, Si₃N₄, and SiO_xN_y films, as well as the electron and hole barriers at the Si/SiO₂, Si/Si₃N₄, and Si/SiO_xN_y interfaces are in good agreement with the experimental findings reported in literatures. © 2009 American Institute of Physics.

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I. INTRODUCTION

Recent progress in theoretical studies of the electronic structure of solids has made the nonempirical *ab initio* calculations of material properties possible. However, when applying the nonempirical methods to calculate the electronic structure of amorphous materials, the computation would involve too much memory storage. It will have great practical values for both material characterization and process optimization if a simple and high-efficient method that is able to predict the material properties of amorphous solids is available. Tight-binding method has been recognized as one of the most powerful methods for this purpose.^{1–3} In this work, we propose a simple physical method for calculating the electronic structure of amorphous materials. A remarkable feature of this method is that it does not involve any adjustable fitting parameters. As will be shown later, this method is a high-efficient theoretical approach for predicting the physical properties of materials such as amorphous silicon oxide (SiO₂), amorphous silicon nitride (Si₃N₄), and amorphous silicon oxynitride (SiO_xN_y), which have an ion-covalent type of binding.

Silicon oxide has been used as the gate dielectric in metal-oxide-semiconductor (MOS) devices for several decades. It was then replaced with SiO_xN_y, which has the advantages of both SiO₂ and Si₃N₄ films such as higher dielectric constant and better hardness for hot carrier irradiation.^{4–7} According to some recent projections,^{7,8} SiO_xN_y will remain in use for some high-performance and low-power logic applications. Silicon oxynitride is also used as the tunneling dielectric in Flash memory devices.⁹ The contents of nitrogen and oxygen in a SiO_xN_y film can vary freely between constraints of the end members: SiO₂ and Si₃N₄, for tailoring the physical and electrical properties of the film. For instance, the low-frequency dielectric constant of SiO_xN_y may vary from 3.9 (SiO₂) to 7.0 (Si₃N₄).¹⁰ The higher the content

of Si–N bonds, the higher the dielectric constant is. Similarly, the bandgap energy of SiO_xN_y may vary from 8.0 eV (SiO₂) (Ref. 10) to 4.5 eV (Si₃N₄).⁴ The electron and hole barriers at the Si/SiO₂ interface are $\phi^e=3.14$ eV and $\phi^h=3.8$ eV, respectively.¹¹ A material with a higher nitrogen content would have smaller barrier values and the lower bounds are $\phi^e=2.0$ eV and $\phi^h=1.5$ eV, which are the barrier heights at the Si/Si₃N₄ interface.^{12,13} However, the low barrier heights of Si/SiO_xN_y structure would lead to undesirable large amount of charge carrier injection in MOS devices. Thus, the composition of SiO_xN_y has to be optimized to meet the device requirements. With this connection, a high-efficient theoretical calculation tool that is able to accurately predict the electronic structure of the oxynitride in different compositions would help in both the device characterization and material optimization.

The conventional *ab initio* quantum-chemical calculation methods fail to produce acceptable bandgap values for most solids. The SiO₂ bandgap energy predicted with the density functional theory (DFT) method was about 5.7 eV, which is significantly smaller than the experimental one (about 8.0 eV).¹⁴ Whereas the Hartree–Fock approximation often overestimates the SiO₂ energy gap to a value of about 17 eV.¹⁴ Better calculation of the bandgap can be done with the recently developed time-dependent DFT method.¹⁵ This work presents an alternate approach to solve this problem. The present paper aims to accurately determine the electronic structure of SiO_xN_y film and the electron and hole barriers at the Si/SiO_xN_y interface by solving the one-electron Green's function with the tight-binding method. The amorphous nature of the films was modeled with the Bethe cluster structure.^{16–18} In this work, we started with the one-electron tight-binding-like Hamiltonian $\sum_{X\alpha,Y\beta} H_{X\alpha,Y\beta} \hat{c}_{X\alpha}^\dagger \hat{c}_{Y\beta} + \text{H.c.}$ The conventional approach to construct this matrix is as follows. The diagonal and off-diagonal matrix elements, $H_{X\alpha,Y\beta}$, were determined by fitting the band structure with data from either experiments or other calculations,¹⁹ or through proper estimation from parameters available in other

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materials with similar structure.^{3,19–21} Unlike the conventional approaches, the matrix elements $H_{X\alpha, Y\beta}$ in this work were solely determined from the atomic properties of lattice atoms.²² No any fitting was made. This method is presented in Sec. II where a heuristic process for determining the diagonal and off-diagonal elements will also be given. Experimental validations of the proposed method will be presented in Sec. III.

II. THEORY

The diagonal elements, $H_{X\alpha, Y\beta}$, for the X th lattice site or atom with a basis function of the α th type can be expressed as

$$H_{X\alpha, X\alpha} = W_{X\alpha} + U_{X\alpha} - T_{X\alpha}, \quad (1)$$

where $W_{X\alpha}$ are the diagonal elements for isolated atoms (with one-electron atomic level), and $T_{X\alpha}$ and $U_{X\alpha}$ are the changes, respectively, in the intra-atomic kinetic energy and in the additional Coulomb repulsion energy due to the overlapping of electron shells and the change in electron localization in the solid. These energy changes can be represented as

$$U_{X\alpha} = U_{X\alpha}^0 \left(\frac{a_{X\alpha}^0}{a_{X\alpha}} \right), \quad T_{X\alpha} = T_{X\alpha}^0 \left(\frac{a_{X\alpha}^0}{a_{X\alpha}} \right)^2, \quad (2)$$

where $a_{X\alpha}^0$ is the initial radius of the α th orbital of the X th atom, and $a_{X\alpha}$ is the radius of the same orbital in the solid. The quantities $U_{X\alpha}^0$ and $T_{X\alpha}^0 = (1/2m)(\hbar/a_{X\alpha}^0)^2$ are governed by the characteristics of the isolated atoms. The actual values of $W_{X\alpha}$ and $U_{X\alpha}^0$ can be found in Ref. 23.

The orbital radii, $a_{X\alpha}$, are a function of the ionic radii, a_X , of the elements forming the solid material. Additionally, the value of $a_{X\alpha}$ can be borrowed from *ab initio* molecular calculations or obtained from experiments on materials with integer value of atomic charges. Here, we use a quadratic interpolation based on the charge states of the atom, namely,

$$a_X = a_{0X} + a_{1X}\delta n_X + a_{2X}(\delta n_X)^2, \quad \delta n_X = \sum_{\alpha} n_{X\alpha} - Z_X, \quad (3)$$

where δn_X is the change in the number of electrons localized on the X th atom in the solid. Z_X is the number of electrons in the valence shell of an isolated atom and $n_{X\alpha}$ is the actual value of the occupation number of the α th type atomiclike basis orbital.

The off-diagonal matrix elements, $H_{X\alpha, Y\beta}$, were calculated as a linear combination of the two centerlike parameters³

$$V_{X\alpha, Y\beta} = \pm \sqrt{T_{X\alpha} T_{Y\beta} n_{X\alpha} n_{Y\beta}} = \pm \frac{\hbar^2}{2ma_{X\alpha} a_{Y\beta}} \sqrt{n_{X\alpha} n_{Y\beta}}, \quad (4)$$

where the occupation numbers are given by

$$n_{X\alpha} = \langle \hat{n}_{X\alpha} \rangle = \langle \hat{c}_{X\alpha}^+ \hat{c}_{X\alpha} \rangle = - \int_{-\infty}^{E_F} \frac{1}{\pi} \text{Im} G_{X\alpha, X\alpha}(E + i0) dE. \quad (5)$$

$G_{X\alpha, X\alpha}(E + i0)$ in Eq. (5) are the diagonal matrix elements of the one-electron Green function and can be found from the following system:

$$\sum_{Z, \gamma} [(E + i0)\delta_{X, Z}\delta_{\alpha, \gamma} - H_{X\alpha, Z\beta}] G_{Z\gamma, Y\beta}(E + i0) = \delta_{X, Y}\delta_{\alpha, \beta}. \quad (6)$$

The elements in Eq. (4), with the use of Slater–Koster³ notation, can be presented in a more familiar form: $V_{X\alpha, Y\beta} = V(l_X l'_Y m) = (l_X l'_Y)_m$; $l, l' = s(0), p(1), d(2)$, etc.; $m = m' = \sigma(0), \pi(1), \delta(2)$, etc. Here the subscripts l, l' , and $m = m'$ represent the angular parts $Y_l^m(\theta, \varphi)$ of the atomiclike basis functions.

The four sp^3 hybrids on each of the Si atoms (i.e., the $2px, 2py$, and $2pz$ oxygen orbitals and one oxygen $2s$ orbital) and the three sp^2 and so called π orbital of p electrons of nitrogen were included in the basis set of orbital. The last item included in the basis set is equivalent to the s, p valence shell from every type of atoms.

A self-consistent approach is needed for solving Eqs. (1)–(6). For the case of crystal lattice, the system can be solved numerically by using the \mathbf{k} -space representation. The problem has been well defined but still requires a good deal of programming work. For disordered and amorphous materials, approximation must be made. One of the successful approximations is the cluster-Bethe lattice method.¹⁶ In short Bethe lattice is a bonded network with a tree topology. There is no any ring bonding in this kind of structure. The geometry of nearest neighbor and the local environment of an atom are considered as the same as those in a real solid. The theoretical results based on this trivial topology had showed excellent agreement with the experimental results for materials with some disorders.^{3,19,20}

An ideal amorphous silicon oxynitride film is normally treated as a continuous network of Si atoms, which are randomly bounded to neighbor oxygen and nitrogen atoms. That is, the material structure can be modeled with a random Bethe lattice²⁴ with Si–O bonding probability p and Si–N bonding probability $1-p$. The $a\text{-SiO}_x\text{N}_y$ film can be treated as a set of five random clusters: $\text{SiO}_\nu\text{N}_{4-\nu}$ ($\nu = 1, 2, 3, 4$). The distribution of the clusters in the film is assumed to follow the binomial law, i.e.,

$$W_\nu(p) = C_4^\nu p^\nu (1-p)^{4-\nu}. \quad (7)$$

To compare the theoretical results with the experimental data, the averaged Green's function and the dependence of the probability p on the compositions x and y must be known. The only yet nontrivial assumption used in the approach is that the probability p is directly governed by the composition parameter $\delta = x/(x+y)$; that is, $p = \delta$ and the δ values can be obtained from the ellipsometric measurements on oxynitride films. This approach was reported in Ref. 19. The diagonal matrix elements (over the lattice sites or atoms) of the Green function of the effective medium can be expressed in terms of the effective-medium parameters, $\sigma_{j(X)}^X(E, p)$, by

$$G_{XX}(E, p) = \left(IE - H_{XX} - \sum_j \sigma_{j(X)}^X(E, p) \right)^{-1}, \quad (8)$$

where $X = \text{Si}, \text{N}, \text{O}$. According to the coordination numbers of the bracketed atoms, $j(\text{Si}) = 1, 2, 3, 4$; $j(\text{N}) = 1, 2, 3$; and $j(\text{O}) = 1, 2$. G_{XX}, H_{XX} , and $\sigma_{j(X)}^X$ are $M \times M$ matrices, and $M(X)$ is the number of the basis orbital of the lattice site or

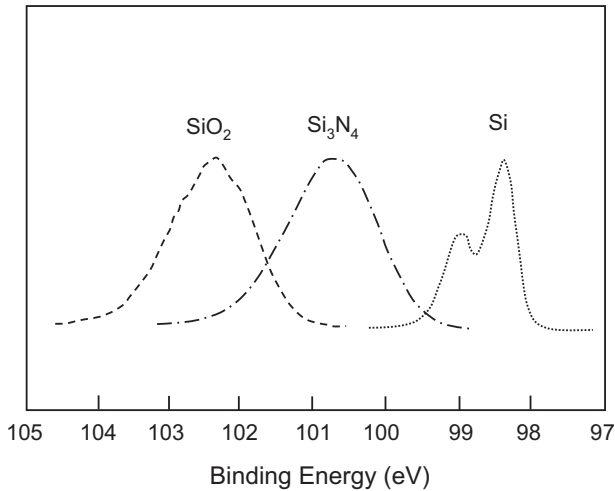


FIG. 1. Experimental x-ray photoelectron spectra of the Si 2*p* core level in Si, Si₃N₄, and SiO₂.

atom, X . These parameters can be determined in a self-consistent manner.¹⁹ Note that here we have only one independent parameter $\sigma_{j(\text{Si})}^{\text{Si}}(E, p)$ at $j(\text{Si})=1$. All other parameters are determined according to the tetrahedral symmetry for Si atom coordination. The calculation results are discussed in Sec. III.

III. EXPERIMENTAL VALIDATION

To determine the charge on the Si atoms in the dielectric films, various dielectric films were prepared. The SiO₂ film was thermally grown on a Si substrate where the Si₃N₄ and α -SiO_{*x*}N_{*y*} films were deposited using chemical vapor deposition method.⁶ These films are about 5 nm thick. The film thickness and the refractive index were measured on a single wavelength ellipsometer equipped with a He–Ne laser with a wavelength of 6328 Å. It was found that the refractive index of α -SiO_{*x*}N_{*y*} is a function of $\delta=x/(x+y)$. X-ray photoelectron spectroscopy (XPS) measurements were conducted with a Kratos AXIS-HS system using monochromatized Al $K\alpha$ as the excitation source.

Figure 1 shows the XPS of Si 2*p* core level in Si, Si₃N₄, and SiO₂ films. The energies of Si 2*p* levels are 98.7, 100.8, and 102.4 eV in Si, Si₃N₄, and SiO₂, respectively. The chemical shift of the Si 2*p* level depends linearly on the positive charge on Si atoms, Q^{Si} . The Si atoms in a silicon material should be neutral because of the covalent nature of the Si–Si bonds. The charge on oxygen atom, Q^{O} , in amorphous SiO₂ was determined experimentally with the positron annihilation and is $-1.0q$ (here q is the charge of free electron).²⁵ Since the O atom in SiO₂ is twofold-coordinated by Si atom, the charge transfer per Si–O bond (Δ^{SiO}) is $0.5q$. On the other hand, as the Si atom in SiO₂ is fourfold-coordinated by O atoms, Q^{Si} in SiO₂ is then $+2.0q$. The positive charge in Si atom in Si₃N₄ film calculated from the chemical shift is $+1.40q$. In addition, since the Si atom in Si₃N₄ is fourfold-coordinated by N atoms, the charge transfer per Si–N bond (Δ^{SiN}) is $0.35q$. Meanwhile, the negative charge on nitrogen atom (Q^{N}) in Si₃N₄ is $-1.05q$ as the nitrogen atom is

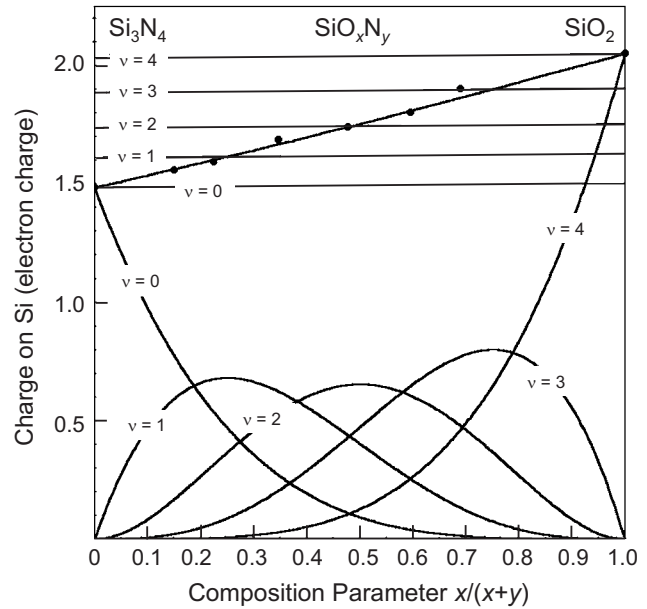


FIG. 2. Bottom: Distribution function of SiO_{*v*}N_{4-*v*} tetrahedral multiplied by the charge on Si atom plotted as a function of the chemical composition of the film. Top: Charge on Si atom being averaged over all configurations of the tetrahedral. The markers are experimental data taken from the report by Vogl *et al.* (Ref. 21) and curves are the theoretical results based on present calculations.

threefold-coordinated by Si atom. Our theoretical values, $Q^{\text{Si}}=2.05$ for SiO₂ and $Q^{\text{Si}}=1.48$ for Si₃N₄, are in good agreement with the aforementioned values.

Figure 2 shows the calculated charges on the central Si atom (q_v) in SiO_{*v*}N_{4-*v*} clusters embedded in the effective Bethe lattice, for various compositions of silicon oxynitride. The dots show the charge values extracted from the Si 2*p* chemical shift in XPS spectra.⁶ The lines in the upper part of the figure indicate the calculated charge on Si atom for various silicon oxynitride films. One can see the excellent agreement between the experimental and the calculated results. The near horizontal lines at the top of the figure for different v values indicate that the charge on the central Si atom of a SiO_{*v*}N_{4-*v*} cluster is almost independent of the environment. Also note that the charge values, which are averaged values over a macroscopic region according to the distribution function $W_v(\delta)$, are almost linearly scaled by the δ values.

Figure 3 shows the calculated values for the top of the valence band, E_V , and the bottom of the conduction band, E_C . These energies were calculated as a function of refractive index by using the experimental dependence of refractive index on δ .¹⁰ The calculation results agree well with experimental data from various sources.^{13,26–30} Based on this result, one can readily estimate the position of E_C and E_V , and then the electron and hole barriers of a SiO_{*x*}N_{*y*} film once its refractive index is known.

IV. CONCLUSION

In summary, we calculated the electronic structure of ion-covalent amorphous dielectrics SiO₂, Si₃N₄, and SiO_{*x*}N_{*y*} by using an improved method. In the proposed model, we used some well-known characteristics of isolated atoms and no fitting parameter from the experimental results is re-

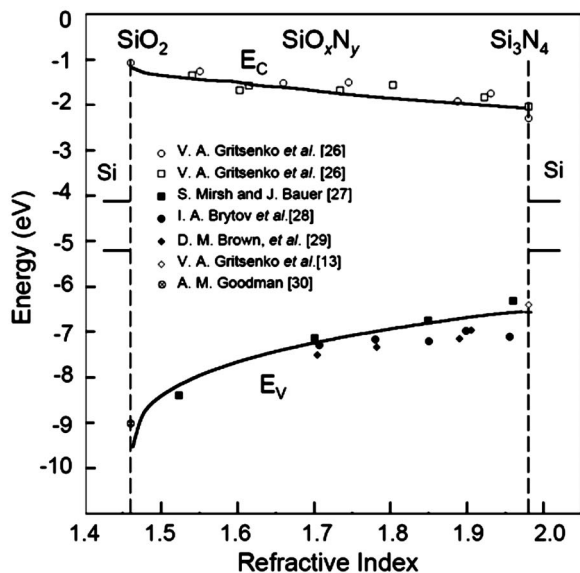


FIG. 3. The energy positions of the top of the valence band (E_V) and the bottom of the conduction band (E_C) in the SiO_xN_y films with different compositions. The curves are the present calculation results and the markers are the experimental data taken from various sources: one-electron photoemission from Si (Ref. 25), two-electron photoemission from Al in MOS devices (Ref. 26), three-optical absorption (Ref. 26), four-optical absorption (Ref. 27), five-optical absorption (Ref. 28), and hole photoemission from Si (Ref. 29).

quired. We found that the charges on Si atoms for the end members of oxynitride, i.e., SiO_2 and Si_3N_4 , are $2.05q$ and $1.48q$, respectively. These results agree well with the actual values of $2.00q$ and $1.40q$. In addition, the calculated curve of the atomic charge versus the composition parameter $\delta = x/(x+y)$ also shows a fairly good agreement with the experimental ones.

The calculated electronic energy structure, in particular, the bandgap energy and the band edge positions with respect to the vacuum level, agrees well with the experimental data from various sources. A slight difference was found at the top of the valence band of SiO_2 . This difference seems to be arising from some of the assumptions made in the present model such as there are no close rings in the Bethe lattice and the tetrahedral and dihedral angles were fixed in the simplified model.

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