Short Range Order and the Nature of Defects and Traps in Amorphous Silicon Oxynitride Governed by the Mott Rule

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Using valence band and Si $2p$ core level photoelectron spectroscopy, it is shown that the short range order in amorphous silicon oxynitride (a-SiO_xN_y) is governed by the Mott rule. According to this rule, each Si atom is coordinated by four O and/or N atoms, each O atom (as in SiO_2) is coordinated by two Si atoms, and each N atom (as in Si_3N_4) is coordinated by three Si atoms. The nature of the removal of Si-Si bonds (hole traps) at the interface of SiO_2/Si by nitridation and the origin of Si-Si bond creation near the top surface of gate oxynitride in metal-oxide-semiconductor devices are understood for the first time by the Mott rule. [S0031-9007(98)06731-3]

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Short range order in tetrahedral solids such as Si, SiO_2, crystalline α-Si_3N_4 and β-Si_3N_4, amorphous silicon nitride a-Si_3N_4, and crystalline silicon oxynitride c-Si_2N_2O is described by the Mott rule as

$$N_C = 8 - n\,, \tag{1}$$

where N_C is the coordination number and n is the number of valence electrons [1–3]. The Si atom has four valence electrons ($3s^2 3p^2$), and according to Eq. (1), its N_C is equal to 4. The O atom has six valence electrons ($2s^2 2p^4$). Therefore, in SiO_2 and c-Si_2N_2O, each O atom is coordinated by two Si atoms. Similarly, the N atom has five valence electrons ($2s^2 2p^3$), and in Si_3N_4 and c-Si_2N_2O, each N atom is threefold coordinated by Si atoms. The amorphous silicon oxynitride (a-SiO_xN_y) of different compositions (from SiO_2 to Si_3N_4) consists of Si-O and Si-N bonds and involves five types of tetrahedra $SiO_\upsilon N_{4-\upsilon}$ for $\upsilon = 0, 1, 2, 3, 4$. The distribution of a particular tetrahedron $SiO_\upsilon N_{4-\upsilon}$ with υ configuration for composition (x, y) is given by random statistics

$$w(\upsilon, x, y) = \left(\frac{2x}{2x + 3y}\right)^{\upsilon} \left(\frac{3y}{2x + 3y}\right)^{4-\upsilon} \frac{4!}{\upsilon!\,(4 - \upsilon)!}\,. \tag{2}$$

Previous studies showed that the short range order in a-SiO_xN_y is generally governed by the Mott rule. But at some composition of a-SiO_xN_y a deviation from the Mott rule by up to 5 at. % was observed [1]. The nature of this deviation is still unclear, so the validity of the Mott rule is under question. More fundamentally, the defect creation in solids is an important chemical and physical process, the understanding of which is basic to our knowledge of solid states. A relevant example is the defect creation in a-SiO_xN_y.

There is a great interest in using a-SiO_xN_y as gate dielectric in future nanoscale metal-oxide-semiconductor (MOS) silicon devices to replace SiO_2 [4–7]. The a-SiO_xN_y combines the advantages of SiO_2 (low density of surface states and high barriers for injection of electron and hole at the interface with Si) and Si_3N_4 (high atomic density and dielectric permittivity). A major advantage of using a-SiO_xN_y is the removal of Si—Si bonds at the SiO_2/Si interface [8]. The Si—Si bonds are hole traps and result in the degradation of the electrical properties of SiO_2/Si due to the accumulation of positive charges [9]. The a-SiO_xN_y gate dielectric is produced by annealing SiO_2/Si in nitrogen containing gases (NH_3, NO, N_2O). This process removes hole traps (Si-Si bonds) from the Si/SiO_2 interface [9,10]. The nature of this phenomenon is so far unclear [5,9–11]. Furthermore, $\equiv Si_3N$ species are observed at the top surface of the gate SiO_xN_y [5]. The annealing of SiO_2 in NH_3 creates a high density of electron traps in SiO_xN_y. To reduce the trap density, the reoxidation of SiO_xN_y has been used after nitridation. Reoxidation can reduce the electron trap density and regrow SiO_2 on the top surface of SiO_xN_y. However, at the top surface of SiO_xN_y a high density of hole traps are regained [9–12]. These traps are also due to the Si-Si bonds, which has been found from the electron-spin-resonance (ESR) experiments showing a high density of paramagnetic E' centers at the top interface of SiO_2/SiO_xN_y [9]. The E' center is created after a hole captured by an Si-Si bond according to the reaction: $\equiv$Si—Si$\equiv$ + h $\rightarrow$ $\equiv$Si$\bullet$ + Si$\equiv$. Thus the ESR data show that the Si-Si bonds exist at the SiO_2/SiO_xN_y interface. The origin of the hole traps due to Si-Si bonds at the top SiO_2/SiO_xN_y interface is not clear yet. The aim of the present paper is to verify quantitatively the Mott rule applicability for chemical bonds in a-SiO_xN_y of different compositions, in order to understand the nature of defects and traps in gate oxynitride on the atomic scale.

The a-SiO_xN_y films of different compositions (thickness about 1000 Å) were prepared on silicon (100) substrates by low-pressure chemical vapor deposition from SiH_4, NH_3, and O_2 at 875 °C. We used x-ray

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photoemission spectroscopy (XPS) to determine the a-SiO_xN_y composition and infrared spectroscopy to detect the concentration of hydrogen bonds. For XPS measurements, the samples were dipped into a solution of 1:30 HF/deionized water to remove surface oxide. In the present study, we used thermal SiO_2 and a-Si_3N_4 as standards for a-SiO_xN_y composition determination. ESR measurements were made at room temperature using a Bruker 300X spectrometer in X band at power of 5 μW.

Valence band XPS specta of SiO_2, Si_3N_4, and a-SiO_xN_y films of different compositions are shown in Fig. 1. The a-SiO_xN_y valence band consists of three subbands. The analysis of ionization cross sections of O $2s$, N $2s$, O $2p$, N $2p$, Si $3s$, Si $3p$ states [13] at an excitation energy of 1486.6 eV shows that the main contribution to the subbands at 19 and 22 eV is from the

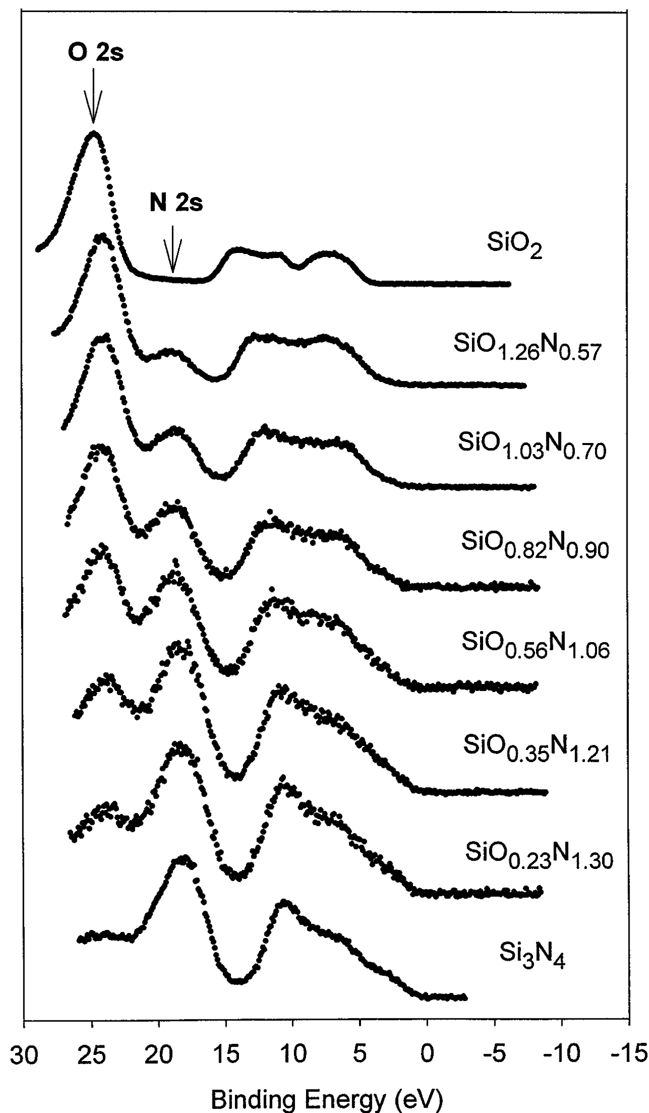


FIG. 1. XPS valence band spectra of a-SiO_xN_y for different compositions. The energy zero point corresponds to the top of the Si_3N_4 valence band.

O $2s$ and N $2s$ states, respectively, and the top subband at 0–13 eV comes mostly from Si $3s$ and Si $3p$ states.

The experimental valence band XPS, ultraviolet photoelectron spectra (UPS) of a-$SiO_{0.56}N_{1.06}$ and x-ray emission of Si $L_{2,3}$, Si K_β, N K_β, and O K_β spectra of a-$SiO_{0.4}N_{1.1}$ are shown in Fig. 2. The main contribution to the UPS is from the O $2p$ and N $2p$ states. Si $L_{2,3}$ emission originates from the transition of the valence Si $3s$ and $3d$ states to the core Si $2p$ state, and Si K_β is due to the transition from the valence Si $3p$ state to the core Si $1s$ state. In the first approximation, the Si $L_{2,3}$ emission spectrum reflects the Si $3s$, $3d$ partial density of states (PDOS) in the valence band, and Si K_β emission spectrum reflects the Si $3p$ PDOS (Fig. 2). Similarly, O K_β and N K_β emission spectra reflect the O $2p$ and N $2p$ PDOS, respectively. When the XPS, UPS valence spectra and x-ray emission spectra are linked together, it can be seen that the top valence subband in the XPS valence spectrum consists of Si $3s$, $3p$, $3d$ states, O $2p$ states, and N $2p$ states. Therefore, Si-O bonds in a-SiO_xN_y are created by O $2s$, $2p$ and Si $3s$, $3p$, $3d$ bonding states, and Si-N bonds are created by N $2s$, $2p$ and Si $3s$, $3p$, $3d$ bonding states. The presence of Si $3d$ states near the c-Si_2N_2O top of the valence band was shown by

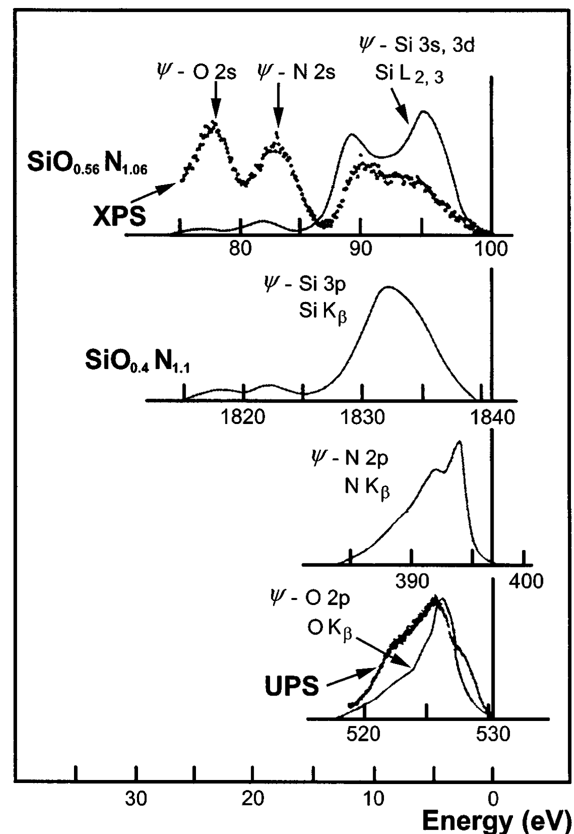


FIG. 2. Valence band XPS, UPS (excitation at 40.8 eV) of a-$SiO_{0.56}N_{1.06}$ and Si $L_{2,3}$, N K_β, and O K_β emission spectra of a-$SiO_{0.4}N_{1.1}$. All spectra are combined to the top of the valence band E_v (vertical line). The wave function symmetry is shown on each spectrum.

numerical simulation previously [14]. The above analysis of a-SiO_xN_y valence band electronic structure indicates that electrons in Si $3s$, $3p$, $3d$, N $2s$, $2p$, and O $2s$, $2p$ states form the Si-N and Si-O bonds.

If the short range order in an "ideal" a-SiO_xN_y is governed by the Mott rule, the following relationship must be observed:

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

where x and y are the compositions in the chemical formula. According to the Mott rule in the ideal a-SiO_xN_y, the number of Si bonds must be equal to the total number of N and O bonds.

However, several reasons can be attributed to deviation from the Mott rule. First of all, Eq. (3) assumes that a-SiO_xN_y films do not contain any intrinsic defects, such as $\equiv$Si—Si$\equiv$, $=$N—N$=$. These defects have the coordinated atoms governed by the Mott rule. Moreover, Eq. (2) also assumes that there are no supercoordinated or undercoordinated Si, O, and N atoms, for instance, —O_3Si•, $=N_3$Si•, $\equiv Si_2$N•, $\equiv$SiO•, $=$N•, etc. The symbols —, $=$, $\equiv$, and • mean one single bond, two single bonds, three single bonds, and one unpaired electron, respectively. Also Eq. (3) assumes that there are no extrinsic defects such as $\equiv$SiH, $\equiv Si_2NH$, $\equiv SiNH_2$, and $\equiv$SiOH bonds.

To check the existence of defects we studied ESR and infrared absorption of a-SiO_xN_y. An absorption at 3325 cm^{-1} in infrared absorption spectra was observed, which is attributed to the stretch vibration of the $\equiv Si_2NH$ bond. However, no other hydrogen related extrinsic defects were found. With the known absorption coefficient of the $\equiv Si_2NH$ bond the density of hydrogen bonds was determined [2]. The ESR spectra of the a-SiO_xN_y samples were measured to detect the paramagnetic active defects (dangling bonds). The density of silicon —O_3Si• ($g = 2.00055$), $=N_3$Si• ($g = 2.0028$), and nitrogen $\equiv Si_2$N• ($g = 2.0037$) paramagnetic defects does not exceed 10^{19} per cm^3 [15], which is at least three orders lower than the density of Si-N and Si-O bonds.

The accuracy of Eq. (3) was verified by plotting $4/(2x + 3y)$ versus $x/(x + y)$, where $x/(x + y)$ characterizes the chemical composition of the a-SiO_xN_y films. A deviation of about 9% from the Mott rule can be found from the plot (see Fig. 3). However, when the concentration of hydrogen bonds [NH] was taken into account for each sample, the plot of $4/(2x + 3y\text{-[NH]})$ versus $x/(x + y)$ deviates from the Mott rule less than 2%, which is the accuracy of a-SiO_xN_y composition determination by XPS. The obtained results show that the Mott rule governs the short range order in a-SiO_xN_y for all the compositions ranging from SiO_2 to Si_3N_4.

The Mott rule which governs the short range order in a-SiO_xN_y is the key to explaining the origin of defects and traps in gate oxynitride. The removal of hole traps from the SiO_2/Si interface during the oxide nitridation

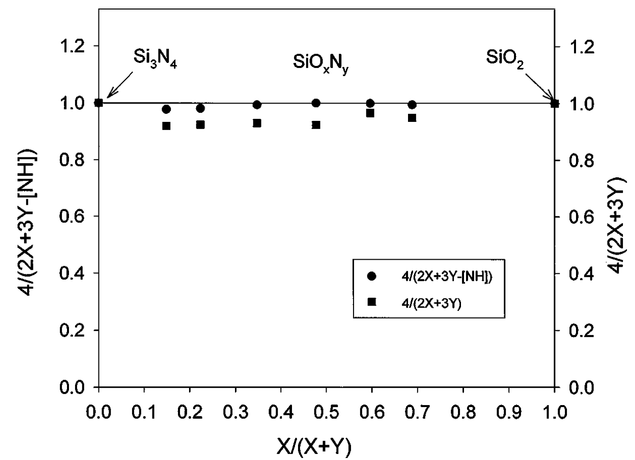
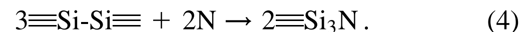


FIG. 3. Experimentally determined relationship of the number of silicon bonds versus the sum of nitrogen and oxygen bonds in a-SiO_xN_y for different compositions. (■) without hydrogen bonds (●) with hydrogen bonds.

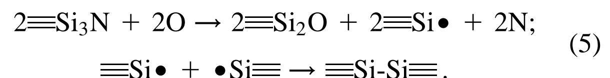
can be understood from the reaction



$$3{\equiv}\text{Si-Si}{\equiv} + 2\text{N} \rightarrow 2{\equiv}\text{Si}_3\text{N}. \tag{4}$$

The coordination number of N is 3, so the interaction of two N atoms with three Si-Si bonds creates two $\equiv Si_3N$ species [5].

Furthermore, the hole traps near the top surface of gate oxynitride are related to $\equiv$Si-Si$\equiv$ bonds which are created by the oxidation of nitride species $\equiv Si_3N$, as shown in the following reaction:



$$\begin{gathered} 2{\equiv}\text{Si}_3\text{N} + 2\text{O} \rightarrow 2{\equiv}\text{Si}_2\text{O} + 2{\equiv}\text{Si}\bullet + 2\text{N}; \\ {\equiv}\text{Si}\bullet + \bullet\text{Si}{\equiv} \rightarrow {\equiv}\text{Si-Si}{\equiv}. \end{gathered} \tag{5}$$

According to Eq. (5), the creation of hole traps (Si-Si bonds) during reoxidation of SiO_xN_y is related to the replacement of N atoms by O atoms [16].

The Si-Si bonds are electron and hole traps in SiO_2. This is found from the experimental work [17] and numerical simulation by quantum-chemical method MINDO/3 [18,19]. The polaron model of electron and hole captured by the Si-Si bonds via multiphonon process in Si_3N_4 has been proposed and developed [2,19–23]. According to these results, the Si-Si bonds act as electron and hole traps at the Si_3N_4/SiO_2 interface. Equation (5) explains the abnormally large number of hole and electron accumulations at the Si_3N_4/thermal oxide interface due to the creation of Si-Si bonds during Si_3N_4 oxidation [24,25].

The validity of the Mott rule for SiO_xN_y opens up the possibility of proposing the more specific definition of point defects in an amorphous solid by Elliott [26]. A *point defect* is any deviation from the coordination number described by the Mott rule and from the expected sort of atoms in formation of the bonds with respect to an ideal (defect-free) structure. In the case of SiO_2 and Si_3N_4 this definition includes paramagnetic defects such

as ≡Si•, ≡Si-O-O•, $\equiv Si_2N$•, diamagnetic defects such as ≡Si-Si≡, =N-H, two coordinated Si-atom with lone pair electrons =Si: (sililene center in SiO_2 [27]), neutral defects such as ≡SiO•, =Si:, ≡SiOH, charged defects such as ≡Si• $^+$Si≡ (E' center in SiO_2), intrinsic defects such as ≡Si•, =N-N=, ≡Si-O-O-Si≡, and extrinsic defects such as ≡SiH, $\equiv Si_2NH$, ≡SiOH.

In conclusion, the validity of the Mott rule for a-SiO_xN_y of different compositions in the range from SiO_2 to Si_3N_4 was experimentally verified by investigating valence band electronic structures and by quantitative analysis of the chemical compositions. This observation contributes to our understanding of the fundamental rule, which dominates short range order and defect creation during chemical reactions in tetrahedral amorphous solids, e.g., SiO_xN_y, SiN_x, and SiO_x. The nature of the removal of Si-Si bonds (hole traps) at the interface of SiO_2/Si by nitridation and the origin of Si-Si bond creation of gate oxynitride in MOS devices are for the first time understood on the basis of the Mott rule in a-SiO_xN_y.

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