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Atomic and Electronic Structures of Traps in Silicon Oxide and Silicon Oxynitride

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Atomic and Electronic Structures of Traps in Silicon Oxide and Silicon Oxynitride

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Silicon oxide (SiO₂) and silicon oxynitride (SiOₓNᵧ) are key materials used in silicon devices. The excellent interface properties of these dielectrics with silicon have enabled the tremendous advancement of metal-oxide-semiconductor (MOS) technology. However, these dielectrics are still found to have pronounced amount of localized states which act as electron or hole traps and lead to the performance and reliability degradations of the MOS integrated circuits. A better understanding of the nature of these states will help to understand the constraints and lifetime performance of the MOS devices. Recently, due to the availability of *ab initio* quantum-mechanical calculations and some synchrotron radiation experiments, substantial progress has been achieved in understanding the atomic and electronic nature of the defects in these dielectrics. In this review, the properties, formation and removal mechanisms of various defects in silicon oxide and silicon oxynitride films will be critically discussed. Some remarks on the thermal ionization energies in connection with the optical ionization energies of electron and hole traps, as well as some of the unsolved issues in these materials will be highlighted.

**Keywords** dielectric traps, electronic structures, silicon oxide, silicon oxynitride, gate dielectrics

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**1. INTRODUCTION**

Silicon oxide (SiO$_2$) and silicon oxynitride (SiO$_x$N$_y$) had been the key dielectrics in silicon integrated circuit technology (IC) technology for many decades. Because of their low density of states and large band offset energies when interfacing with the silicon substrate together with the high dielectric breakdown field, they had been used as the gate dielectrics for metal-oxide-semiconductor (MOS) transistors for many decades. However, the low densities of oxide charge and interface trap still caused some pronounced performance and reliability degradations of the MOS devices and had attracted much attention in the past few decades. The charges injected into these dielectrics would result in the charge trapping and cause threshold voltage shift in the MOS transistors. The requirement for operational stability of a MOS transistor is rather stringent in the modern MOS technology because of the small device size, large system scale, and long (10 years) operation lifetime. For instance, the threshold voltage shift of MOS transistors in a microprocessor should not exceed 10 mV for a 10-year continuous operation. Yet the significance of using these dielectrics in the MOS devices has been reduced recently, but the instability issues of these dielectric films become even more important. In the state-of-the-art nanoscale MOS technology, the gate dielectric has been replaced by a higher dielectric constant (high-k) material such as Al$_2$O$_3$ (k ≈ 10), HfSiO$_x$ (k ≈ 15), HfO$_2$N$_y$ (k ≈ 15), HfAlO$_x$ (k ≈ 15), HfO$_2$ (k ≈ 25), and ZrO$_2$ (k ≈ 25) in order to have better control of the channel current with the desirable gate voltages and to suppress the gate leakage current. However, high-k materials are often found to have poor interface properties with silicon substrate. With this connection, an ultrathin layer (about 0.5 nm thick) of thermal oxide or oxynitride was grown before the high-k deposition. Thus, the quality of this ultrathin silicon oxide or oxynitride layer would have even greater impact on the reliability of MOS integrated circuits.

A better understanding of the electronic properties of silicon oxide is also important to the IC fabrication process. One of the important methods for making the advanced silicon-on-insulator (SOI) wafers is the SIMOX (separation by implantation of oxygen) process. In this process, the initial Si wafer was implanted with a high dose (>$10^{18}$ cm$^{-2}$) of high-energy (>100 keV) oxygen ions so as to form a thick buried oxide layer. To re-crystallize the implanted surface, high-temperature post-implantation annealing needed to be conducted. As will be discussed later, this process would result in the generation of oxygen vacancies and give rise to some instability issues for devices and circuits fabricated on it.

On the other hand, silicon oxide and oxynitride are still widely used as tunneling oxide in memory devices. A flash memory element comprises a MOSFET whose threshold voltage can be changed in a write cycle by injecting electrons or holes over the tunneling oxide into the storage medium such as floating polysilicon or silicon nitride with high amount of deep traps. However, the charges accumulated on the electron or hole traps of the tunneling oxide can cause an undesirable threshold shift of the memory transistors and results in the performance degradation of the flash memory. In addition, the high field writing process also results in the generation of new electron and hole traps in the tunneling oxide. This trap generation normally involves some weak bonds or electrically inactive defect precursors in the dielectrics produced during the fabrication process. Finally, silicon oxide and silicon oxynitride are also used as core and cladding material for glass fibers and micro wave guiding devices. The charge trapping causes optical loss and needs to be minimized.

Hence, a better understanding of the properties, the formation and the removal mechanisms of the dielectric traps will help the process engineers to characterize and to improve the fabrication of these dielectric films. It will also help the device engineers to understand the constraints, the performance, and probably to predict the degradation behaviors and then the lifetime, of devices as far as charge trapping events are involved. A systematic survey on the defect properties of oxynitride was presented. In recent years, substantial progress in the understanding the atomic and electronic structure, and formation mechanisms, of defects in silicon oxide and oxynitride had been achieved with the help of theoretical non-empirical *ab initio* quantum-mechanical calculations and some synchrotron experiments. The purpose of this review is to provide a readily accessible archive that highlights the important results, in
relation to the atomic and electronic structure of intrinsic defects in silicon oxide and silicon oxynitride, reported recently.

2. THE MOTT OCTAHEDRAL RULE IN TETRAHEDRAL SILICON-BASED COMPOUNDS

The atomic bonding in a solid is governed by the Mott rule which relates the coordination number (CN) in a solid with its number of valence electrons (n), i.e.,

\[ CN = 8 - n \]  

As a Si atom has four valence electrons given by \( s^2p^2 \), each Si atom in the Si crystal, SiO\(_2\), or Si\(_3\)N\(_4\) would occupy one site in the tetrahedral coordination and is coordinated to four silicon, four oxygen, or four nitrogen atoms, respectively, in these substances. An oxygen atom has six valence electrons \( (s^2p^3) \), thus each oxygen atom bridges with two silicon atoms in SiO\(_2\). A nitrogen atom has five valence electrons \( (s^2p^3) \) and hence it is connected to three Si atoms in the Si\(_3\)N\(_4\). Silicon oxynitride consists of both Si-O and Si-N bonding. It was shown that in a broad range of compositions, from SiO\(_2\) to Si\(_3\)N\(_4\), Si-O and Si-N bonds in silicon oxynitride form five types of tetrahedral \((\text{Si}_n\text{O}_m\text{N}_8, \nu = 0, 1, 2, 3, 4)\) and the distribution of these tetrahedrons is governed by the binomial distribution function.\(^{13,14}\) In line with the Mott octahedral rule, in Si\(_2\)O\(_n\), each oxygen atom bridges with two Si atoms, similar to that in SiO\(_2\), and each nitrogen atom is coordinated by three Si atoms as similar to Si\(_3\)N\(_4\). The Mott rule provides a clue to understand the atomic structures and the formation mechanisms of defects or traps in silicon-based tetrahedral compounds. Based on the Mott rule, Gritsenko and coworkers\(^{13}\) proposed a definition of a perfect material. That is, if a compound that did not contain any defect deviating from regular coordination numbers of the containing atoms, then the material is said to be defect-less.\(^{13}\)

According to this definition, defects in SiO\(_2\), Si\(_3\)N\(_4\), and Si\(_n\)O\(_m\)N\(_y\) can be exemplified by (a) paramagnetic centers such as \( \equiv\text{SiO} \equiv\), \( \equiv\text{SiOO} \equiv\), and \( \equiv\text{SiN} \equiv\); (b) diamagnetic centers such as \( \equiv\text{Si-Si} \equiv\), \( \equiv\text{Si} \equiv\); (c) neutral defects include \( \equiv\text{SiOH} \equiv\), \( \equiv\text{Si-Si} \equiv\), and \( \equiv\text{Si} \equiv\); (d) charged defects \( \equiv\text{SiO}^\dagger \equiv\) and \( \equiv\text{Si}^\dagger \equiv\); (e) intrinsic defects \( \equiv\text{SiOO}^\dagger \equiv\), \( \equiv\text{SiN}^\dagger \equiv\), and \( \equiv\text{Si-Si}^\dagger \equiv\); and (f) impurity defects \( \equiv\text{Si}_2\text{NH} \equiv\), \( \equiv\text{SiOH} \equiv\), and \( \equiv\text{SiH} \equiv\). In the above designations, the notation \( (\cdot) \) denotes a regular chemical bond formed by two electrons with opposite spin directions, and the notation \( (\cdot) \) denotes an unpaired electron. Detail structures, characteristics and formation mechanisms of these defects will be discussed in Sections 3 to 8. A summary together will some further remarks will be given in Section 9.

3. OXYGEN VACANCY

3.1. Atomic and Electronic Structures of Neutral Oxygen Vacancy

The oxygen vacancy, \( \equiv\text{Si-Si} \equiv\), or Si-Si bond in short, in silicon oxide can be formed on the removal of an oxygen atom from the Si-O-Si bridge according to the following reaction:

\[ \equiv\text{Si-O-Si} \equiv \rightarrow \equiv\text{Si-Si} \equiv + \text{O} \]  

An oxygen vacancy can also be formed when an oxygen atom jumped to the neighbor site during the formation of peroxide radical \( \equiv\text{Si-O-Si} \equiv\), i.e.,

\[ \equiv\text{Si-O-Si-O-Si} \equiv \rightarrow \equiv\text{Si-Si-O-Si} \equiv \]  

It was reported that the inter-atomic distance between the Si atoms in the Si-O-Si bond in amorphous SiO\(_2\) is 3.05 Å\(^{14}\) and the equilibrium length of the neutral \( \equiv\text{Si-Si} \equiv \) bond in SiO\(_2\) is about 2.5 Å\(^{15-17}\) which is slightly larger than the length of the Si-Si bond (2.35 Å) in amorphous silicon. Mukhopadhyay et al.\(^{18}\) examined the length distribution of neutral Si-Si bonds in amorphous silicon oxide and found that it varies from 2.3 to 2.7 Å.

The oxygen vacancy in silicon oxide is a neutral diamagnetic center. The electronic structure of the neutral O\(_2\)\( \equiv\text{Si-Si} \equiv\)O\(_3\) bond in SiO\(_2\) was examined by quantum-mechanical calculations.\(^{15-20}\) The binding \( \sigma^*\)-orbital in the Si-Si bond are found to lie close to the top of the valence band, whereas the antibinding \( \sigma^\ast\)-orbital are 7.6 eV above the energy position of the binding orbital. A binding \( \sigma\)-orbit is occupied by two electrons with opposite spins whereas the antibinding \( \sigma^\ast\)-orbit is empty. Similar absorption peak at 7.56 eV was also found in disilane molecule \( \text{Si}_2\text{H}_6 \) which has a Si-Si bond in it.\(^{21}\)

According to the quantum-mechanical calculations, the Si-Si defect in SiO\(_2\) gives rise to an absorption band at 7.6 eV. By performing thermal annealing of quartz glass in a hydrogen ambient, Hosono, Abe, and Imagawa et al. suggested that this band should be due to the Si-Si bonds.\(^{22}\) Figure 1 shows the absorption spectra of SiO\(_2\) samples annealed in hydrogen at 1000°C in hydrogen for 1 hour (solid curve), with 800°C annealing in hydrogen for 1 hour (dotted curve). (Reprinted with permission from Hosono et al.\(^{22}\) Copyright 1991: American Physical Society.)
ambient. The absorption at 7.6 eV became weaker after hydrogen annealing. However, the reduction in the absorption at 7.6 eV was found to be less pronounced at an annealing temperature of 800°C than the one annealed at 1000°C. An explanation to this behavior was proposed.\textsuperscript{22} It was found that the reduction of the 7.6-eV absorption band was accompanied by an increase of the IR absorption at 2260 cm\textsuperscript{-1} due to vibrations of Si-H bonds (see Figure 2). Electron paramagnetic resonance (EPR) study showed that no EPR signal due to S-Si bonds was observed in both non-annealed and hydrogen-annealed samples. These experimental findings suggest that the reduction in the absorption intensity at 7.6 eV was due to the broken of Si-Si bonds for hydrogen incorporation via the following reaction:

\[ \equiv\text{Si-Si} + \text{H}_2 \rightarrow \equiv\text{Si-H} + \text{H-Si} \equiv \]  \[\text{[4]}\]

This reaction explains the increase of the absorption at 2260 cm\textsuperscript{-1} because of the increase in Si-H bond density. Based on the quantitative analysis on the absorption due to Si-Si and Si-H bonds, a linear correlation between the 7.6 eV absorption and 2260 cm\textsuperscript{-1} band was obtained.\textsuperscript{22} And this correlation further suggests that the 7.6-eV absorption band in SiO\textsubscript{2} is due to the excitation of electron from the $\sigma$ binding orbital to $\sigma^*$ antibinding orbital of the Si-Si bond. This conjecture is further confirmed by experiments conducted in oxygen-rich oxide film.\textsuperscript{23} As shown in Figure 3, for samples being annealed in oxygen, the intensity of the 7.6-eV absorption band was reduced. This behavior can be attributed to the reduction of Si-Si bond concentration as a result of oxidation, i.e.,

\[ 2\equiv\text{Si-Si} + \text{O}_2 \rightarrow 2\equiv\text{Si-O-Si} \equiv \]  \[\text{[5]}\]

By exciting a quartz glass with a light source within the 7.6 eV absorption band, a photoluminescence (PL) band peaking at about 4.4 eV emerges.\textsuperscript{24–26} Figure 4 shows the PL spectrum of a quartz sample and the suggested the configuration diagram for explaining the optical transitions with 7.6 eV PL excitation is shown in Figure 5. The large Stokes shift suggests a strong electron-phonon coupling during the optical transitions in the Si-Si bonds. According to the configuration diagram, the Franck-Condon shift, or the polaron energy, amounts to $W_p = (7.6 - 4.4)/2 = 1.6$ eV. As will be discussed later on, this polaron energy coincides well, within the experimental accuracy, with the energy of the electron and hole traps in SiO\textsubscript{2}.

3.2. Formation Mechanism of Si-Si Bonds in Silicon Oxide

The oxygen vacancy in silicon oxide was observed in samples irradiated with ions, neutrons, photons, or $\gamma$ quanta.\textsuperscript{27} Hosono and Matsunami\textsuperscript{28} showed that Si-Si bonds formed in SiO\textsubscript{2} layers with Li\textsuperscript{+}, N\textsuperscript{+}, O\textsuperscript{+}, F\textsuperscript{+}, Si\textsuperscript{+}, or P\textsuperscript{+} ions implantation. Si-Si bonds are formed in SiO\textsubscript{2} with ion irradiation via reaction (2). The existence of the Si-Si bonds can be detected through the observation of the 7.6 eV optical absorption.\textsuperscript{28}

Garrido et al. used x-ray photoelectron spectroscopy (XPS) to investigate the radiation defects in SiO\textsubscript{2} films by using Ar\textsuperscript{+} ion irradiation.\textsuperscript{29} In the irradiated samples, a broadening of the Si 2p atomic level towards the lower binding energy side, accompanied with a decrease of the signal intensity, was observed (see Figure 6). A similar phenomenon was also observed in Si-rich SiO\textsubscript{x} films.\textsuperscript{30,31} SiO\textsubscript{x} consists of five type of tetrahedral: SiO\textsubscript{4}, SiO\textsubscript{3}, SiO\textsubscript{2}, SiO, and Si\textsubscript{0} bonding state and each oxygen atom in the SiO\textsubscript{x} bridges with two Si atoms. In SiO\textsubscript{2}, the oxygen and silicon atoms carry -1.0e and +2.0e charges, respectively. Thus the net charge transfer per one Si-O bond is equal to 0.5e.\textsuperscript{32} The broadening of the Si 2p peak in irradiated silicon oxide with a large irradiation dose (see Figure 6) can be attributed to the increase of number of tetrahedral with larger amount of Si-Si bonds.

It was found in a 230 nm thick wet oxide with 50 keV B\textsuperscript{+} ion irradiation that the IR vibrational spectra exhibited several significant changes.\textsuperscript{31} By increasing the irradiation dose, a red shift and peak broadening the absorption were observed. The red shift of the absorption maximum was due to the replacement of Si atoms in the SiO\textsubscript{2}, tetrahedral with O atoms. In quartz samples with B\textsuperscript{+} ion implantation, red shift of the fundamental absorption edge was also found\textsuperscript{33} A similar behavior was also observed in Si-rich SiO\textsubscript{x} films.\textsuperscript{31,34} The red shift of the fundamental absorption edge in SiO\textsubscript{x} can also be attributed to the increase of Si-Si bond concentration. That is, the IR spectroscopy, the photoelectron spectroscopy, as well as the optical absorption spectra all together confirmed that oxygen vacancies will be formed in ion-irradiated silicon oxide films.
ATOMIC AND ELECTRONIC STRUCTURES OF TRAPS IN SILICON OXIDE AND SILICON OXYNITRIDE

FIG. 3. Infrared absorption spectra of SiO$_{1.98}$ samples annealed in oxygen at different temperatures. (Reprinted with permission from Hikmott, Copyright 1971: American Institute of Physics.)

FIG. 4. Photoluminescence spectra due to 7.6-eV excitation and the photoluminescence excitation spectra (PLE) of quartz glasses irradiated with neutrons. The spectra were measured at 15 K. (Reprinted with permission from Gee and Kastner, Copyright: American Physical Society.)

Figure 7 shows the XPS spectra of a 6 Å thick SiO$_2$ layer grown on a (100) Si substrate. The excitation source was synchrotron radiation with an energy of 130 eV. The spectra were registered at two synchrotron radiation angles: 0° and 60°.

FIG. 5. Configuration diagram for optical transitions of defects in SiO$_2$ as a result of photoluminescence excitation with energy in the 7.6 eV absorption band.
FIG. 6. Photoelectron spectra of the Si 2p level in as-grown (trace a) and 130-keV Ar$^+$ ion irradiated with dose of $3.2 \times 10^{13}$ cm$^{-2}$ (trace b), $3.2 \times 10^{14}$ cm$^{-2}$ (trace c), and $3.2 \times 10^{16}$ cm$^{-2}$ (trace d). The vertical line shows the position of the Si 2p level in Si. (Reprinted with permission from Garrido et al. 29 Copyright: Elsevier.)

This thickness is in the range of thinnest bulk silicon oxide that often used as inter-layer for other kinds of dielectrics deposited on silicon. 6 In the spectra given in Figure 7, the energy is reckoned from the position of the atomic Si 2p peak in the Si substrate (SiSi4 tetrahedron). The peak at the energy of 26.5 eV is due to the SiSi4 tetrahedral in the Si substrate and the shape of this peak is defined by the spin-doublet splitting. The Si4$^+$ peak at 23 eV is due to the SiO4 tetrahedral in the stoichiometric SiO2. In addition to these peaks, three peaks, due to Si3$^+$, Si2$^+$, and Si$^+$ were observed at intermediate energies which were resulted, respectively, from the suboxides, SiSiO3, SiSi2O2, and Si3SiO tetrahedral presented at the Si/SiO2 interface. These experiments unequivocally imply the presence of excess silicon in thermal oxide in the vicinity of Si/SiO2 interface. The observation of SiSiO3 tetrahedral implies the presence of O≡Si-Si≡O3 bonds (oxygen vacancies) in the samples, while the existence of SiSi2O2 tetrahedral is an indication of the presence of oxygen divacancies O≡Si-Si≡Si≡O2. That is, an oxide film should contain some excess silicon atoms in the vicinity of Si/SiO2 interface. An independent confirmation for the existence of excess silicon in the form of O≡Si-Si≡O2 and O≡Si-Si≡Si≡O3 defects was done by Naga, Miyata, and Moriki et al. 36 For thermally grown oxide films with 14–45 Å thick, synchrotron radiation tests on the films yield some similar optical absorption bands. As mentioned earlier, the O≡Si-Si≡O3 defects in SiO2 exhibit an absorption band at 7.6 eV. 15-17 Figure 8 shows the optical absorption spectra of some thin thermal oxides on silicon extracted from the measured reflectance spectra. The absorption at 7.8 eV due to Si-Si defects is obvious and the estimated concentration for this defect is about $8 \times 10^{14}$ cm$^{-2}$. Additional absorption at 6.5 eV, related to the oxygen divacancy, is also observed.

3.3. Neutral Oxygen Vacancy as a Hole Trap

When a hole is captured by a $\equiv$Si-Si$\equiv$ bond, an E$'$ center forms:

$$\equiv$Si-Si$\equiv$ + h $\rightarrow$ $\equiv$Si$^+$Si$\equiv$ . \[6\]

This positively-charged paramagnetic defect, $\equiv$Si$^+$Si$\equiv$, has an unpaired electron. There exists a whole family of E$'$ centers. 37 Note that the above definition for the E$'$ center is not unique. Sometimes a threefold-coordinated Si atom with an unpaired electron, $\equiv$Si$-$, is also considered as an E$'$ center. The electronic structure of E$'$ has been a hot subject for theoretical studies. 15,17,19,38-41 When a hole is captured by a $\equiv$Si-Si$\equiv$ bond, the positively charged silicon atom, $^+$Si$\equiv$, shifts towards the plane where the three oxygen atoms lie, while the paramagnetic silicon atom with an unpaired electron, $\equiv$Si$-$, shifts towards the positively-charged silicon atom side (see Figure 9). 17

The hole trapping mechanism of Si-Si oxygen vacancy was confirmed experimentally by Withan and Lenahan. 42 Figure 10
shows the capacitance-voltage (C-V) characteristics of a MOS structure. It demonstrated that the hole injection caused the C-V characteristics being shifted to the negative side. The positive charges accumulated in the oxide results in an EPR signal with gyromagnetic factor \( g = 2.0004 \). This EPR signal was identified as arising from the hole trapping at Si-Si bonds according to reaction (6).

Electron injection into oxide leads to the neutralization of the positive charges and makes the EPR signal to be disappeared (see Figure 10). Figure 11 shows the surface density of \( E' \) centers as a function of trapped hole surface density. The slope of the curve indicates that the positive charge of \( E' \) centers. Layer-by-layer etching experiments showed that most of the \( E' \) centers were localized in the oxide near the Si/SiO\(_2\) interface. Figure 12
FIG. 8. Optical absorption spectrum of thermal oxide on Si showing shoulder energies of 6.5 eV, 7.8 eV, and 8.8 eV. (Reprinted with permission from Terada et al.36 Copyright 1992: American Physical Society.)

plots the density of the $E'$ centers and the flat-band voltage as a function of annealing temperature during isochronal annealing.43 The dotted curve in Figure 12 shows the kinetic data for $E'$ centers in the annealed samples and the activation energy of the process falls in the range of 1.0 to 1.8 eV according to the first-order kinetics given below:

$$N = N_0 \exp[-\nu t \exp(-W_t/kT)]$$  

where, $W_t$ is the trap activation energy, $t$ is the annealing time, and $\nu$ is the frequency factor. Expression (7) yields a stronger dependence in comparison with the experiments. The experimental data, however, can still be fitted fairly well with expression (7) by assuming a Gaussian distribution of activation energies:

$$\rho(W) = \frac{1}{(2\pi)^{1/2}} \exp[-(W - W_t)^2/\Delta W^2] \quad [8]$$

Figure 12 also shows the predicted dependence calculated by using $W_t = 1.6$ eV, $\Delta W = 0.3$ eV, and $\nu = 10^{13}$ sec$^{-1}$.

The energy spectrum of hole traps in SiO$_2$ was also studied. The activation energy of a hole trap ($W_h$) was found to be about 1.44±0.2 eV which was determined from the threshold voltage versus temperature plot.44 In this work, we assumed $\nu = 10^{14}$ sec$^{-1}$, the energy of the hole trap of about 1.6 eV can be obtained from Equ. (7). This value coincides with the polaron energy obtained from luminescent data taken from samples with excited Si-Si bonds (see Figure 5).

Miller et al.45 examined the energy distribution of hole traps in a 350 nm thick thermal silicon oxide by using thermally stimulated current measurements. Two peaks were observed in the hole trap distribution. By assuming $\nu = 10^{14}$ sec$^{-1}$ in their work, the high-energy peak is at about 1.85 eV, whereas the low-energy peak is at about 1.2 eV. Figure 13 shows the energy distribution of hole traps in thermal silicon oxide.45 The high-energy peak due to hole emission from oxygen vacancies is at about 1.5 eV and the low-energy peak which is tentatively attributed to the emission of holes from oxygen divacancies is at about 0.9 eV.

Manzini and Modelli examined the tunneling ionization of hole traps in silicon oxide.46 By assuming the hole mass of $m_h^* = 0.42 m_0$, the energy of the hole trap in thermal silicon oxide ($W_{h\text{ opt}}$) was estimated to be 3.1 eV. According to the multi-phonon trap ionization theory, the energy for tunneling ionization should be equal to the optical energy, $W_{h\text{ opt}}$.47 Thus the optical ionization energy should be about twice of the thermal ionization energy, i.e., $W_{h\text{ opt}} \approx 2 W_t$. A similar relation for optical and thermal ionization energies of hole traps was also observed in amorphous silicon nitride Si$_3$N$_4$.48 Figure 14 shows the field dependence of the hole capture cross-section of neutral traps (Si-Si bonds).49 As the electric field in the oxide increases from $10^5$ to $5 \times 10^6$ V/cm, the capture cross-section decreases from $10^{-12}$ cm$^2$ to $10^{-13}$ cm$^2$.

Powell and Berglund50 used the internal photoemission method to investigate the spatial localization of positively-charged traps in oxide layers. It was found that the Si-Si bonds were localized in silicon oxide layers at a distance of about 2 nm from the Si-SiO$_2$ interface. It can be deduced that most of the oxygen vacancies (Si-Si bonds) in the thermal oxide layers should be localized within a thin interfacial region near the Si substrate. The presence of oxygen vacancies near the interface is an intrinsic property of thermal silicon oxide. Oxygen vacancies and divacancies, or excess silicon, are formed due to the insufficient oxidation as a result of less sufficient supply of oxygen species which diffuse from the surface during the thermal oxidation of process.

Oxygen vacancies (Si-Si bonds) were also found in SIMOX structures which were produced by oxygen ion implantation.
following with a high-temperature annealing. Paullet et al. examined the charge accumulation in Si/SiO$_2$/Si structures with a 200 nm thick oxide layer being annealed at 1320°C in inert gas. The oxide layer was then irradiated with an x-ray after the covering polysilicon layer was removed. By plotting the accumulated charge density as a function of the irradiation dose, the hole capture cross-section of the neutral trap was determined and the value is about $3.6 \times 10^{-13}$ cm$^2$. This result suggested that the oxygen vacancy is also an intrinsic defect in the oxide of SIMOX structures. The formation of oxygen vacancies can be attributed to reaction (2) taken place during the high-temperature annealing in inert gases. Note that both electron and hole accumulations were observed in MOS structures with Si$^+$ ion implantation into the gate oxide. Figure 15 shows the
kinetics of electron and hole accumulation in a MOS structure with $3 \times 10^{16}$ cm$^{-2}$ Si ions being implanted into the gate oxide. Here the threshold voltage of the MOSFET was measured as a function of the pulse width for charge pumping measurements. The accumulated charge density increases with both the pulse width and amplitude, in the similar manner as those in metal-oxide-nitride-oxide-metal (MONOS) structures.

3.4. Formation of Si-Si Bonds in Re-oxidized Silicon Oxynitride

When a silicon oxide film was treated in ammonia, doubly-coordinated nitrogen atoms $= SiN\cdot$ which act as electron traps
will be formed (see Section 8). To remove these traps, the sample can be re-oxidized with process as given in Equ (9). It was found that the E' centers were still found on the outer surface of re-oxidized nitrided oxide films.52 This is an indication of the formation of Si-Si bonds on the outer surface also. Mallik et al.53 showed that some hole traps with an abnormally large capture cross-section, about $7.9 \times 10^{-12}$ cm$^{-2}$, were formed on the surface of re-oxidized nitrided oxide films. On the other hand, Gritsenko et al.54 showed that in oxidizing silicon nitride, Si-Si bonds can be formed at the Si$_3$N$_4$/SiO$_2$ interface via the following reactions:

$2 \equiv Si\equiv + 2O \rightarrow 2\equiv SiO\equiv + 2\equiv Si\equiv + 2N\equiv$, \hspace{1cm} [9]

$\equiv Si\equiv + \equiv Si\equiv \rightarrow \equiv Si-Si\equiv$. \hspace{1cm} [10]

It suggests that the Si-Si bonds will be formed by converting the Si-N bonds via the oxidation reactions given in Equ. (9) and (10) during the re-oxidation of the nitrided oxide films.

3.5. Positively Charged Oxygen Vacancy as an Electron Trap

The electron capture cross-section for a positively-charged trap in an As$^+$ ion irradiated oxide was examined.55 The irradiation leads to the formation of oxygen vacancies according to Equ. (2). Charging of the E' centers in the irradiated SiO$_2$ was obtained by injecting holes from the silicon substrate. The positively-charged E' centers can trap electrons. By injecting electron with internal photoemission technique, the following reaction takes place:

$\equiv Si\equiv + e \rightarrow \equiv Si-Si\equiv$. \hspace{1cm} [11]

that is, the electron capture of a positively-charged E' center would lead to the formation of neutral oxygen vacancy, or Si-Si bond. Figure 16 shows the electron capture cross-section of E' centers at room temperature as a function of electric field.55 The cross-section decreases from about $10^{-12}$ cm$^2$ at electric field of $2 \times 10^5$ V/cm to about $3 \times 10^{-15}$ cm$^2$ at a field strength of $2 \times 10^6$ V/cm. In Figure 16, it also shows the Monte-Carlo simulation data based on some classical and quantum models.55

3.6. Neutral Oxygen Vacancy as an Electron Trap

A neutral oxygen vacancy in SiO$_2$ can trap both electron and hole. The electron trapping properties of oxygen vacancies in silicon oxide films with As$^+$ ion irradiation was examined.55 Figure 17 shows the field dependence of the electron capture cross-section of Si-Si bonds. Within the experimental accuracy, the capture cross-section is in the order of $10^{-15}$ cm$^2$ and does not depend on the electric field.55 The hole capturing properties of the neutral Si-Si defects were also examined with quantum-chemical calculations.38 It was found that the Si-Si defect acts as a hole trap with energy of $0.7 \pm 0.5$ eV. DFT method was also used to investigate into the electron capture capability of the Si-Si bonds.13,52 It was found that the Si-Si defect can also function as an electron trap and the trap energy was reported to be 1.7,56 and 2.3 eV. On the other hand, it was found experimentally that the electron capture cross-section is in the range of $10^{-15}$ to $10^{-14}$ cm$^2$ according to the thermal and optical delocalization experiments of the trapped electrons (presumably, Si-Si bonds).57,58 The thermal ionization energy was found to be equal to $W_t = 1.7 \pm 0.2$ eV. The trap energy obtained from
Fig. 17. Field dependence of electron capture cross-section of neutral Si-Si bonds. (Reprinted with permission from Buchanan et al. Copyright 1991: American Physical Society.)

...the formation of Si-Si bonds give rise to an electron trapping in this material. However, an abnormally large value of the electron capture cross-section of about 1.5 × 10^{-13} cm^2 was observed. This value is close to the electron and hole capture cross-section in amorphous silicon nitride. It can be speculated that the giant electron capture cross-section in SiO_2 might be due to, as in nitride Si-rich SiN_x, the splitting of antibonding orbital in Si-Si bonds. In nitride SiN_x with excess silicon, the electron and hole capture cross-section of neutral traps are about 5 × 10^{-13} cm^2.

4. Oxygen Divacancy

4.1. Atomic and Electronic Structure of Neutral Oxygen Vacancy, or \( \equiv \text{Si-Si-Si} \equiv \) Defect

The oxygen divacancy \( \equiv \text{Si-Si-Si} \equiv \) is a diamagnetic defect resulting from the removal of two oxygen atoms from the \( \equiv \text{Si-O-Si-O} \equiv \) chain in SiO_2. Note that in this chain the middle silicon atom is coordinated by four oxygen atoms, of which two are not indicated in this notation. The \( \equiv \text{Si-Si-Si} \equiv \) defect is in a similar configuration to the trisilane molecule Si_3H_8 in gas phase which exhibits a 6.5 eV optical absorption band. According to a quantum-chemical calculation, the oxygen divacancy has an absorption energy of 6.3 eV. The 6.5 eV absorption band observed in the thin thermal oxide layers on Si is a feature of the present of the \( \equiv \text{Si-Si-Si} \equiv \) defects (see Figure 8). The surface concentration of \( \equiv \text{Si-Si-Si} \equiv \) defects in this sample was found to be about 4 × 10^{14} cm^{-2}. An independent confirmation for the existence of the oxygen divacancy in oxide layers near the Si/SiO_2 interface was done by observing the Si^{2+} signal in the Si 2p photoelectron spectra (see Figure 7). In addition, the excitation spectrum of the 4.4 eV PL band in neutron-irradiated quartz samples exhibits a shoulder at 6.7 eV (see Figure 4) which agrees well with the absorption band proposed for the \( \equiv \text{Si-Si-Si} \equiv \) defects. A similar phenomenon was also observed by Nishikawa, Watanabe, and Ito.

4.2. Oxygen Divacancy \( \equiv \text{Si-Si-Si} \equiv \) as a Hole Trap

An EPR study on the atomic and electronic structure of the paramagnetic defects in the Si-rich SiO_x layers was reported. Several values of gyromagnetic (g) factor responding to the different bonding configurations were obtained. g values of 2.0010, 2.0014, 2.0019, and 2.0037, and 2.0055, which respectively correspond to E', E'' center (O_2Si'), oxygen divacancy (O_2SiSi'), oxygen trivacancy (O_3SiSi), and Si_3Si_2, were found. The silicon atom with three-fold coordination to silicon atoms together with an unpaired electron (Si_3Si_2), known as D center was examined in detail in amorphous silicon.

Devine et al. examined the trapping of holes in a Si/SiO_2/Si structure that was annealed at a high temperature of 1320°C in an inert atmosphere. By irradiating the samples with x-rays, γ quanta, ultraviolet, or after hole injection, an EPR signal with g = 2.0019 was observed (see Figure 18). This center is denoted as the E_x center. Within the experimental accuracy, the value of the g-factor for E_x center coincides with that of the oxygen divacancy O_2SiSi'. The oxygen divacancy will be turned into a paramagnetic center after the capture of a hole, i.e.,

\[ \equiv \text{Si-Si-Si} \equiv + h \rightarrow \equiv \text{Si-Si} ^+ \equiv . \]
Conley, Lenahan, Evance et al.,66 and Stesmans67 also reported the similar values of g factor (2.00246 ± 0.00003) for the $E_\delta$ center in thermal oxide. Figure 19 depicts the kinetics for annealing-induced transformation of $E'_\prime$ into $E_\delta$ centers.8 Based on expressions (5) and (6), it can be estimated that $W_t = 1.65$ eV, $\Delta W = 0.15$ eV for the $E'_\prime$ center, and $W_t = 1.33$ eV, $\Delta W = 0.25$ eV for the $E_\delta$ center. The trap energy for the $E'_\prime$ center is close to that extracted from the reported data43 and the result is shown in Figure 12.

The hole trapping in oxygen vacancies and oxygen divacancies at room temperature were also investigated.66 Figure 20 plots the surface density of trapped holes as a function of the number of injected holes per unit area. From these data, the hole capture cross-sections of oxygen vacancy and oxygen divacancy were estimated to be about $3 \times 10^{-13}$ cm$^2$ and $10^{-13}$ cm$^2$, respectively.

4.3. Positively Charged Oxygen Divacancy as an Electron Trap

Conley et al.66 further suggested that an oxygen divacancy with a trapped hole can capture an electron by the following reaction:

$$\equiv \text{Si-Si}^+ \equiv + e \rightarrow \equiv \text{Si-SiSi} \equiv$$  [13]

Figure 21 shows the EPR signal observed after hole and electron injection. The accumulation of holes gives rise to an EPR signal with $g = 2.0019$; this signal vanishes after a subsequent electron injection. Figure 22 plots the trapped charge density as a function of electron fluence.66 From this plot, the electron capture cross-section of oxygen vacancy can be estimated to be in the range of $10^{-14}$ - $10^{-13}$ cm$^2$ and that the oxygen divacancy is in the order of $10^{-12}$ cm$^2$.

5. SILICON CLUSTERS IN SiO$_2$ AS ELECTRON AND HOLE TRAPS

Silicon clusters embedded in SiO$_2$ are used as a charge storage medium in flash memory cells.68 The injection of electrons or holes into these clusters results in the charge localization. EPR results indicate that these clusters behave similar to
some defects in SiO$_2$. By creating silicon nanoclusters with Si implantation into a thick oxide layer with proper annealing, an EPR signal with $g$ factor of $2.0062 \pm 0.0002$ and width of about 0.65 mT was observed (see trace a in Figure 23). These figures indicate the presence of threefold-coordinated silicon atoms with an unpaired electron $\equiv$Si$_3$Si\textsuperscript{·} (D-centers).\textsuperscript{69} After annealing, the radiative defects vanish (see trace b). Injection of electron (trace c) or hole (trace d) results in some new signals responsible to D centers. Figure 24 shows a model for the electron and hole capture in a silicon cluster at the Si/SiO$_2$ interface. After the hole capture, a D center will be formed whereas an electron will be localized at the silicon atom coordinated to three oxygen atoms after an electron capture.

![Fig. 21](image1.png)  
**FIG. 21.** EPR signals due to oxygen divacancy after hole or electron injection. (Reprinted with permission from Conley et al.\textsuperscript{66} Copyright 1994: American Institute of Physics.)

![Fig. 22](image2.png)  
**FIG. 22.** Plot of trapped electron density as a function of electron injection fluence for positively-charged oxygen vacancy and oxygen divacancy. (Reprinted with permission from Conley et al.\textsuperscript{66} Copyright 1994: American Institute of Physics.)

![Fig. 23](image3.png)  
**FIG. 23.** EPR signal of silicon oxide layer with $3 \times 10^{16}$ cm$^{-2}$ silicon implantation. (a) as-grown silicon oxide; (b) sample with Si implantation and post-implant annealing; (c) the implanted sample with electron injection; (d) the implant sample with hole injection.

![Fig. 24](image4.png)  
**FIG. 24.** Model of the silicon cluster/SiO$_2$ interface as a defect for capturing both electron and hole.
6. DOUBLY-COORDINATED SILICON ATOM (≡Si)

The doubly-coordinated silicon atom with two electrons or ≡Si, is a neutral diamagnetic defect that can be formed when two Si-O bonds in a SiO₄ tetrahedron are ruptured, i.e.,

\[ 2≡Si-O-Si≡ → 2≡Si-O· + 2:Si= . \]  

[14]

This defect is also called the divalent center. The divalent center exhibits an absorption band at energy of about 5.0 to 5.2 eV.³⁷ Excitation within this absorption band gives rise to two PL bands at 2.65 to 2.7 and 4.4 eV (see Figure 25). The 2.7 eV PL band has a long lifetime of about 10.2 ms and suggests that the PL is due to an electron transition from the optically excited triplet state into the singlet state.

The electron and hole capture capabilities of the divalent center was also studied.⁷⁰ ⁷¹ It was found that the electron capture in the divalent center is unfavorable, whereas the hole capture may occur via the following reaction:

\[ ≡Si: + h → ≡Si· . \]  

[15]

Figure 26 illustrates the proposed structure of the divalent center in the neutral state. However, the magnitude of the hole capture cross-section of the divalent center is still unknown and no any experimental value for the hole delocalization energy has been reported for this center yet.

7. OXYGEN ATOM WITH AN UNPAIRED ELECTRON (≡Si-O·) AS AN ELECTRON TRAP

The oxygen atom with an unpaired electron is also called oxyradical, or non-bridging oxygen. This defect may arise following the rupture of the \( ≡Si-O-Si≡ \) bond by the reaction below:

\[ ≡Si-O-Si≡ → ≡Si-O· + ·Si≡ . \]  

[16]

Alternatively, an oxyradical may also be resulted from the rupture of the peroxide bridge \( ≡SiOOSi≡ \) as:

\[ ≡SiOOSi≡ → ≡SiO· + ·OSi≡ . \]  

[17]

In silicon oxide films, in particular in silicon oxide produced by wet oxidation, hydrogen bonds in the form of \( ≡SiO· \) defects are commonly found.⁷² The rupture of oxyradical also leads to the formation of \( ≡SiO· \) defect by the following reaction

\[ ≡SiOH → ≡SiO· + H. \]  

[18]

The absorption spectra of the oxyradical has two absorption bands at energies 4.8 and 2.0 eV, respectively.⁷³ A PL band with energy of 1.85 to 1.9 eV can be excited for both bands (see Figure 25). The 2.0 eV absorption band is due to the electron transitions between the O 2p states, which is close to the energy of the top of the valence band of SiO₂.

The charge capture capability of the oxyradical defects in SiO₂ had been examined by semi-empirical method⁷³ and by the non-empirical DFT method using cluster approximation.⁷⁴ Figure 27 illustrates the proposed electronic structure of the oxyradical defect in SiO₂. Hole capture of the oxyradical was shown to be unfavorable from energy point of view. Whereas an electron capture can be occurred via the following reaction:

\[ ≡SiO· + e → ≡SiO: \]  

[19]

According to the data obtained from non-empirical DFT calculations, the energy gain after an electron capture in the oxyradical amounts to 3.9 eV. However, there is no any experimental value for the electron delocalization energy being reported so far. The magnitude of the electron capture cross-section of the oxyradical defect is about \( 1.5 \times 10^{-17} \) cm².⁷⁵
8. DOUBLY-COOORDINATED NITROGEN ATOM WITH AN UNPAIRED ELECTRON, \( \equiv \text{Si}_2\text{N} \cdot \)

As discussed above, in thermal oxide films near the Si-SiO\(_2\) interface, there exist some Si-Si bonds. These Si-Si bonds function as hole traps. The Si-Si bonds can be removed by high temperature annealing in a nitrogen-containing gas, such as ammonia (NH\(_3\)) or nitrous oxide (NO or N\(_2\)O).\(^{76,77}\) The nitrogen atom interacts with an oxygen vacancy via the following reaction:

\[
3 \equiv \text{Si-Si} + 2\text{N} \rightarrow \equiv \text{Si}_3\text{N} \tag{20}
\]

Thus the amount of hole traps would be reduced by converting the Si-Si bonds into Si-N bonds.

Experiments also showed that the nitridation of thermal silicon oxide in ammonia also accompanied with the formation of electron traps.\(^{78-81}\) Ammonia annealing also leads to the removal of Si-Si bonds according to the following reaction

\[
\equiv \text{Si-Si} + \text{NH}_3 \rightarrow \equiv \text{Si}_2\text{NH} + \text{H}_2 \tag{21}
\]

EPR experiments indicated that in silicon nitride and oxynitride there exist doubly-coordinated paramagnetic silicon atoms with an unpaired electron, i.e., \( \equiv \text{Si}_2\text{N} \cdot \) (see Figure 28).\(^{78-81}\) The unpaired electron in the \( \equiv \text{Si}_2\text{N} \cdot \) defect is localized at the antibinding 2\( p_\pi \) orbital of nitrogen. In the antibinding 2\( p_\pi \) orbital of nitrogen, 74 ± 6% of the \( p \)-type wavefunction and 2% of the \( s \)-type wavefunction are localized.\(^{82}\) This kind of defect is formed due to the decomposition of the \( \equiv \text{Si}_2\text{NH} \) defect at high nitridation temperatures (700 to 1000°C) via the following reaction

\[
\equiv \text{Si}_2\text{NH} \rightarrow \equiv \text{Si}_2\text{N} \cdot + \text{H}. \tag{22}
\]

Yount and Lenahan\(^{82}\) showed in oxynitride films with hydrogen annealing that the EPR signal due to the \( \equiv \text{Si}_2\text{N} \cdot \) defects disappears as a result of the hydrogen passivation, i.e.

\[
\equiv \text{Si}_2\text{N} \cdot + \text{H} \rightarrow \equiv \text{Si}_2\text{NH} \tag{23}
\]

Morokov et al.\(^{83}\) examined the electron and hole capturing capability of the \( \equiv \text{Si}_2\text{N} \cdot \) defect based on quantum-chemical calculations and found that this defect would have energy gain on electron capturing but no energy gain for hole capturing. The
electron capture can be described by the following reaction:

\[ \equiv \text{Si}_2\text{N} \cdot + e \rightarrow \equiv \text{Si}_2\text{N} : \]  

The electron capture cross-section of the doubly-coordinated nitrogen atom is about \(10^{-15}\) cm\(^2\). The electron capture results in transforming the defect from the paramagnetic state into the diamagnetic state and the intensity of the EPR signal decreases (see Figure 29). The hole capture in the paramagnetic defect \(\equiv \text{Si}_2\text{N}:\) can be described by:

\[ \equiv \text{Si}_2\text{N}: + h \rightarrow \equiv \text{Si}_2\text{N} \cdot \]  

The \(\equiv \text{Si}_2\text{N} \cdot\) defect can be further removed from silicon oxynitride or nitride film by re-oxidizing the samples in oxygen ambient via the following reaction:

\[ \equiv \text{Si}_2\text{N} \cdot + O \rightarrow \equiv \text{Si-O-Si} \equiv + N \]  

Table 1

<table>
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<tr>
<th>Defect Type</th>
<th>Absorption Band (eV)</th>
<th>Electron Capture cross-section (cm(^2))</th>
<th>Hole Capture cross-section (cm(^2))</th>
<th>Gyromagnetic factor</th>
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<td>(\equiv \text{Si}_2\text{Si}\equiv)</td>
<td>7.56-7.6</td>
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<td>(3 \times 10^{-13})</td>
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<td>(\sim 10^{-12})</td>
<td>(10^{-13})</td>
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<td>unavailable</td>
<td>unavailable</td>
<td>2.0062 ± 0.0002</td>
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<tr>
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<td>(10^{-15})</td>
<td>NA</td>
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</table>

9. SUMMARY

In this work, the formation and the removal mechanisms of various defects, which are defined from the view point of the Mott octahedral rule, in silicon oxide and silicon oxynitride films are critically reviewed. The charge trapping capabilities of these defects are also analyzed in detail. The major properties of these defects are summarized in Table I.

First, the Si-Si bond is a fundamental defect in thermal silicon oxide and has several significant impacts on the operations of MOS devices using silicon oxide or oxynitride as the gate dielectrics. This neutral diamagnetic defect can be formed during the thermal oxide growth or after particle irradiation. The Si-Si bonds can capture both holes and electrons, but the hole capture cross-section of a Si-Si bond is much larger than that of the electron ones. That is why only positive charge accumulation is reported in silicon oxides that were subjected to ionizing irradiation or other treatments giving rise to the generation of hole-electron pairs. This inherent property limits the radiation hardness of silicon oxide films. Here we have presented a detailed discussion on this issue together with some recently reported EPR results. Interestingly, nitridation of silicon oxide in ammonia was found to cause the removal of the interfacial Si-Si bonds and a subsequence re-oxidation of the nitrided oxide can give rise to the formation of Si-Si bonds on the outer surface of the dielectric. A further insight from this review is on the thermal ionization energies of the electron and hole traps of Si-Si bonds in silicon oxide, \(W_e\) and \(W_h\). They are equal and coincide with the Franck-Condon (polaron) shift \(W_p\), i.e., \(W_e = W_h = W_p = 1.6 \pm 0.2\) eV. The optical ionization energies of electron and hole traps, \(W_{opt}^{e}\) and \(W_{opt}^{h}\), are equal too, i.e., \(W_{opt}^{e} = W_{opt}^{h} = 3.0 \pm 0.5\) eV and their values are about twice of the thermal ionization energy, i.e., \(W_{opt}^{e} \approx W_{opt}^{h} \approx 2W_p\). Interestingly, these relations also hold for amorphous silicon nitride.

Second, according to some quantum-chemical calculations, the doubly-coordinated silicon atom with two electrons, or the divalent center, should act as a hole trap in SiO\(_2\). However, no experimental confirmation has been reported so far. This may be due to the small hole capture cross-section of the divalent center and make the probability of hole trapping at divalent centers less significant. This is still an interesting topic worth of further investigation.

Finally, a silicon atom with an unpaired electron or peroxide radical also acts as a hole trap in SiO\(_2\). This center was observed in oxide films grown by wet oxidation. Unlike the dry oxides, wet oxides are more robust against radiation. This property was explained by the partial compensation of the positive charges trapped in the oxygen vacancies and divacancies at the Si/SiO\(_2\) interface with the negative charges trapped at oxygen atoms with an unpaired electron in the bulk of the oxide.

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